

## 1 . PERIODIC PROPERTIES

### 1) Atomic Radius.

Definition:

Is the distance of closest approach of one atom to another atom in a bonding situation.

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

At such a distance, the repulsive forces between nucleus-nucleus, electron-electron and the attractive forces between nucleus-electron just balance.

### Trends in Atomic Radius

I) Across the period.

Atomic radius decreases across the period.

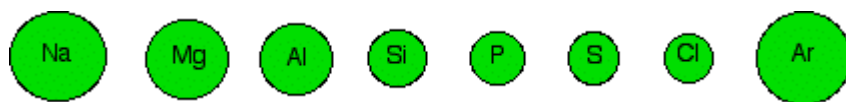
#### Explanation

- On traversing the period from one element to the next, the additional electron is added to shells with the same energy ie no new energy level is formed.
- The nuclear charge progressively increases and yet the screening/ shielding effect of the inner complete shells remains almost constant.
- As a result the effective nuclear charge increases and electrons in the outer most shell are pulled more strongly leading to a decrease in atomic radius.

Elements	At. Number	Electronic configuration
Li	3	$1S^2 2S^1$
Be	4	$1S^2 2S^2$

B	5	$1S^22S^22P^1$
C	6	$1S^22S^22P^2$
N	7	$1S^22S^22P^3$
O	8	$1S^22S^22P^4$
F	9	$1S^22S^22P^5$
Ne	10	$1S^22S^22P^6$

The diagram shows how the atomic radius changes as you go across Period 3.



The figures used to construct this diagram are based on:

metallic radii for Na, Mg and Al;

covalent radii for Si, P, S and Cl;

the van der Waals radius for Ar because it doesn't form any strong bonds.

ii) Down the group

Atomic radius increases down the group in the periodic Table.

#### Explanation

- On descending any group from one element to the next, electrons are being added to shells with higher energies (i.e a new electron shell is formed)
- As a result both the nuclear charge and screening effect increase but the increase in screening effect outweighs that due to nuclear charge.
- The effective nuclear charge therefore decreases, nuclear attraction for the outer most electrons decreases hence increase in atomic radius.

Element	Atomic Number	Configuration
Li	3	$1S^2 2S^1$
Na	11	$1S^2 2S^2 2P^6 3S^1$
K	19	$1S^2 2S^2 2P^6 3S^2 3P^6 4S^1$
Rb	37	$1S^2 2S^2 2P^6 3S^2 3P^6 4S^2 3d^{10} 4P^6 5S^1$
Cs	55	-----

### Cations

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

#### Explanation

After the removal of one or more electrons, the number of protons in the nucleus become greater than the number of remaining electrons, thus the proton-electron ratio increases.

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

### Anions

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

#### Explanation

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

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

## Isoelectronic ions

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

**For example:**

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

**isoelectronic ions,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{F}^-$  (ions both have 10 electrons):**

- $\text{Al}^{3+}$  has 13 protons, a nuclear charge of +13.
- $\text{Mg}^{2+}$  has 12 protons, a nuclear charge of +12.
- $\text{Na}^+$  has 11 protons, a nuclear charge of +11.
- $\text{F}^-$  has 9 protons, a nuclear charge of +9.

**$\text{Al}^{3+}$ , with the largest nuclear charge will be expected to have the greatest attraction of its electrons .**

**Therefore  $\text{Al}^{3+}$  has the smallest ionic radius i.e radius is in the order  $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$**

**The radius decreases as the positive nuclear charge increases. Consequently charge densities and polarizing powers of the ions increase.**

**Look at the second example of isoelectronic ions,  $\text{S}^{2-}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  (ions all have 18 electrons):**

- $\text{S}^{2-}$  has 16 protons, a nuclear charge of +16.
- $\text{Cl}^-$  has 17 protons, a nuclear charge of +17.
- $\text{K}^+$  has 19 protons, a nuclear charge of +19.

- $\text{Ca}^{2+}$  has 20 protons, a nuclear charge of +20.

## 2. IONISATION ENERGY

The **ionization energy** of an atom measures how strongly an atom holds its electrons.

Definition:

Ionization energy( 1<sup>st</sup> ionization energy) of an element is the minimum amount of energy required to remove an electron completely from the outer most shell of an isolated gaseous atom to form a unipositively charged gaseous ion.



Second ionization energy

Is the minimum amount of energy required to remove an electron from the outer most shell of a unipositively charged gaseous ion to form a dipositively charged gaseous ion.



The higher the value of the ionization energy, the more difficult it is to remove the electron.

As electrons are removed, the positive charge from the nucleus remains unchanged, however, **the ionization energy is higher for each subsequent electron.**

There is also a big increase in ionization energy for removal of an electron from an inner shell (lower  $n$  value).

This is due to the fact that when you move to an orbital with a lower principle quantum number, you are removing an electron which is much closer to the nucleus and is being strongly held by the nucleus.

FACTORS AFFECTING 1<sup>ST</sup> IONIZATION ENERGY

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

Explanation

1. Nuclear charge.

- ✓ When the nuclear charge is high, the electrons present in the outer most shell are attracted more strongly by the nucleus.
- ✓ Therefore removing an electron from this shell requires more energy leading to high 1<sup>st</sup> ionization energy.
- ✓ When the nuclear charge is low, the electrons present in the outer shell are attracted less strongly by the nucleus.
- ✓ Therefore removing an electron from it requires less energy leading to low 1<sup>st</sup> ionization energy.

2. Shielding effect of inner complete shells of electrons.

- This is the tendency of the inner electrons to screen the other outer electrons from the nuclear attraction.
- When the screening effect is high, the effective nuclear charge for the outer most electrons reduces.
- As such less energy is required to remove an electron from the outer most shell leading to low 1<sup>st</sup> ionization energy.
- When the screening effect is low, the effective nuclear charge for the outer most electrons increases.

As a result more energy is required to remove an electron from this outer shell against a high nuclear attraction.

### 3. Atomic radius.

- ✚ If the atomic radius is small, the outer most electrons are closer to the nucleus and are attracted more strongly by it. Thus removing an electron from this outer shell requires more energy leading to high 1<sup>st</sup> ionization energy.
- ✚ If the atomic radius is large, the outer most electrons are more distant from the nucleus. There is less attraction from the nucleus, and an electron can be removed easily leading to a low 1<sup>st</sup> ionization energy.

### 4. Electronic configuration of the outer most shell.

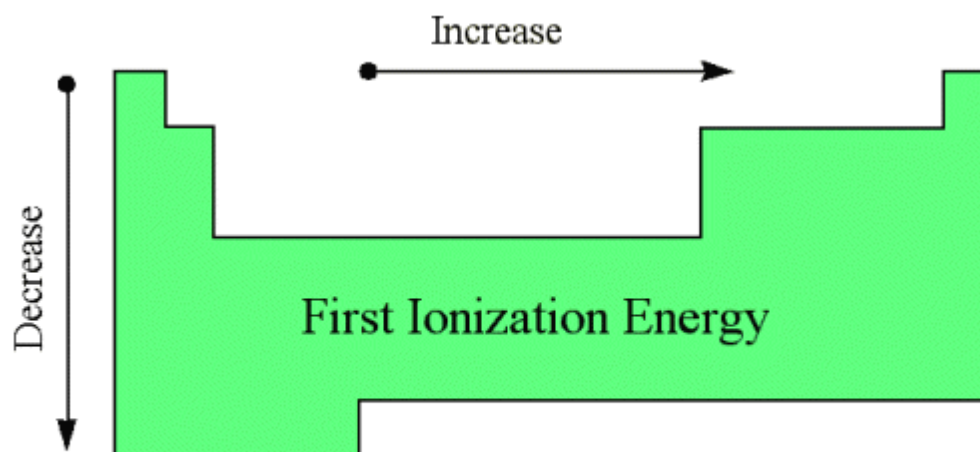
- ✓ When the first electron is coming from an outer sub-shell which is half full (eg. N:  $1S^22S^22P^3$ ), a lot of energy is needed since the unpaired electrons experience minimum repulsion and the shell is thermodynamically stable.
- ✓ When the 1<sup>st</sup> electron is coming from an outer shell which is fully filled e.g Ne:  $1S^22S^22P^6$ , a lot more energy is needed to remove it because the shell is thermodynamically more stable.
- ✓ When the 1<sup>st</sup> electron comes from a shell where electron pairing has begun e.g O: ( $1S^22S^22P^4$ ), less energy is required because of mutual repulsion between paired electrons.

## **Periodic trends in ionization energies**

First ionization energies as a function of atomic number

Within each period (row) the 1<sup>st</sup> ionization energy typically increases with atomic number

Within each group (column) the 1<sup>st</sup> ionization energy typically decreases with increasing atomic number



General trends for the energy required to remove the first electron (first ionization energy) of an element

The basis for these observations:

As the effective charge increases, or as the distance of the electron from the nucleus decreases, the greater the attraction between the nucleus and the electron.

The effective charge increases across a period, in addition, the atomic radius decreases

As we move down a group the distance from the nucleus increases and the attraction of the electrons for the nucleus decreases.

**a) 1<sup>st</sup> ionization energy generally increases across the period in the periodic Table.**

Explanation

On traversing any period in the periodic Table from one element to the next, electrons are being added to shells with the same energy as such the nuclear charge progressively increases while the screening effect of the inner shells remains almost constant.

Consequently, the effective nuclear charge increases leading to a high nuclear attraction for the outer most electrons. Thus removing the 1<sup>st</sup> electron requires more energy.

**b) 1<sup>st</sup> ionization energy generally decreases down any group in the periodic Table.**

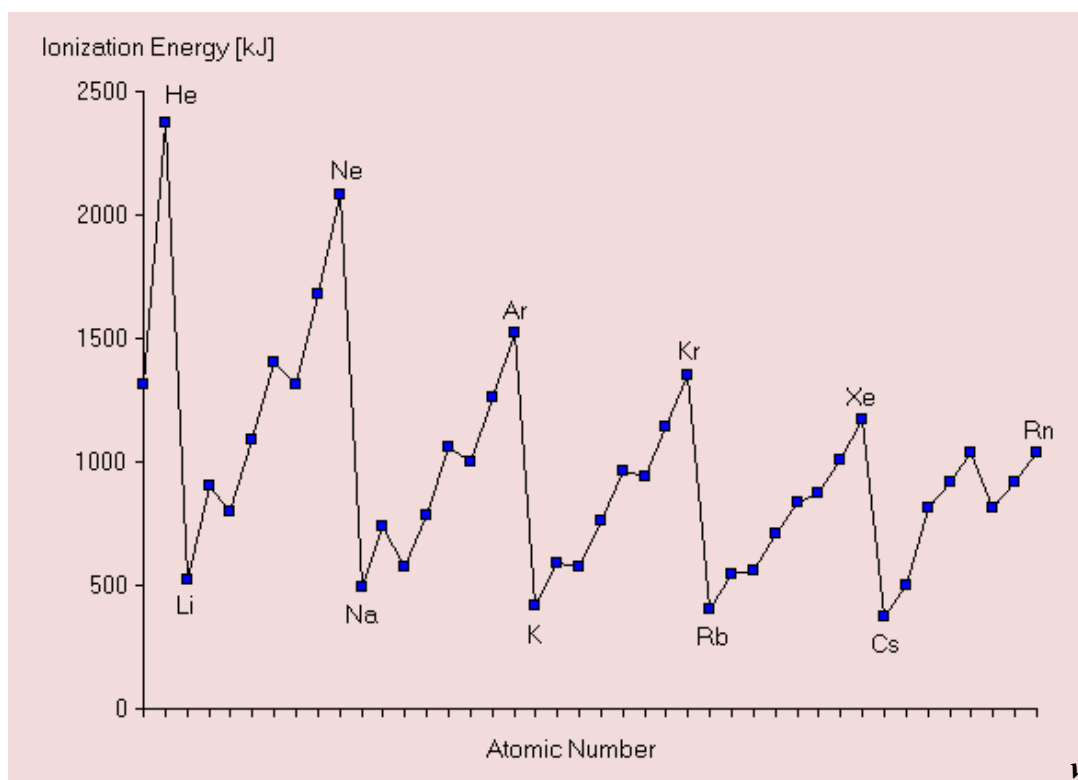
Explanation



On descending any group from one element to the next in the periodic table, electrons are being added to shells with higher energy i.e an extra shell of electrons is added.

Thus both the nuclear charge and the screening effect increase but the increase in screening effect out- weighs that due to nuclear charge.

The effective nuclear charge progressively decreases leading to a decreased nuclear attraction for the outer most electrons hence 1<sup>st</sup> ionization energy decreases.



### Explanation

- ✓ On traversing the short period, lithium to neon, the 1<sup>st</sup> ionization energy increases in general but there is a break observed at boron and oxygen.
- ✓ Lithium,  $1s^2 2s^1$  has the lowest 1<sup>st</sup> ionization energy. This is because the single electron in the outer most 2s shell is weakly held by the nucleus due to the shielding effect of complete inner 1s-electrons.

- ✓ Beryllium,  $1S^22S^2$  has a higher 1<sup>st</sup> I.E because the nuclear charge increases whilst the electron is being added to the same 2s shell. Above all the outer most 2s shell is full.
- ✓ Boron ,  $1S^22S^2 2p^1$  loses the outer most p-electron easily despite an increase in the nuclear charge because the shielding effect of the interposing complete inner s-shells increases thus reducing the effective nuclear charge considerably. In addition, the 2p sub-shell is further from the nucleus than the 2s electron that is removed from Be (1<sup>st</sup> I.E of Be > for B).
- ✓ There after the nuclear charge increases from boron through carbon  $1S^22S^22P^2$  to nitrogen  $1S^22S^22P^3$ , in line with an increase in nuclear charge while electrons are being added to the same shell.
- ✓ At nitrogen, the 2p-subshell is half full, the three electrons being unpaired experience minimum repulsion thus thermodynamically stable.
- ✓ In the case of oxygen  $1S^22S^22P^4$  ,electron is being paired in one of the 2p-orbitals as such there is mutual repulsion between the two paired electrons. An electron can easily be removed from this outer 2p-shell thus a decrease in 1<sup>st</sup> I.E is observed.
- ✓ Further increase in ionization energy is observed on traversing the period from oxygen to neon. This is in line with increase in nuclear charge as the 2p shell is building up and reaches a maximum at neon,  $1S^22S^22P^6$  , which has a complete stable configuration.

A similar trend is observed on traversing the 2<sup>nd</sup> short period from sodium to argon.

NB:

In every period, noble gases have the highest 1<sup>st</sup> ionization energy. This is because noble gases have fully filled outer most shell thus thermodynamically stable.

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

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

Also it has a stable outer most shell  $1s^2$  .

### IMPORTANCE OF IONIZATION ENERGY

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

1. Atomic number of the element .

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

2. The arrangement of electrons in the shells.

A plot of successive ionization energies of calcium shows distinct portions.

Qn.

Element	$1^{st}$ I.E	$2^{nd}$ I.E	$3^{rd}$ I.E	$4^{th}$ I.E
A	800	2400	3700	25000
B	900	1800	14800	21000
C	500	4600	6900	9500
D	1090	2400	4600	6200
E	1310	3400	5300	7500

The table below shows the  $1^{st}$  four ionization energies of elements A-E.

a) Which group in the periodic table does each of the following elements belong:

- i) A            ii) B            iii) C

Give a reason for your answer in each case.

Qn.

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

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

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

b) Which element belongs to :

i) group(i)                  ii) group(ii).

Give reason for your answer in each case.

Qn.

The table below shows the 1<sup>st</sup> five ionization energies in K/J per mole for elements W-Z.

Element	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>
W	577	1816	2745	11575	13251
X	738	1450	7730	10550	12756
Y	495	4563	6912	9540	11936
Z	1255	2297	3849	5163	13989

a) Identify the group to which each of the elements belong and give a reason for your answer in each case.

b) Which pair of elements will form :

i) an ionic bond between them?

ii) a covalent bond?

Qn.

The first 8 ionization energies in K/J per mole of an element Y are shown below:

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

Which group in the periodic table does element Y belong? Give a reason for your answer.

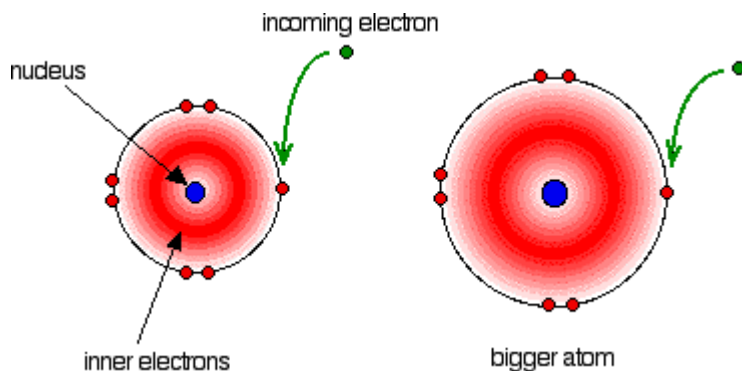
### 3. ELECTRON AFFINITY

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

Electron affinity is defined as the enthalpy change that occurs when a gaseous atom gains an extra electron to form a univalently charged gaseous anion.



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



**First electron affinity:**

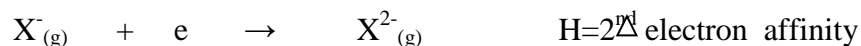
of an element is defined as the energy released when a gaseous atom gains an extra electron to form a univalently charged gaseous anion.



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

**Second electron affinity**

is defined as the amount of energy absorbed/ required when a univalently charged gaseous anion gains an electron to form a divalently charged gaseous anion.



*First electron affinity is an exothermic process .*

Explanation:

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

Second electron affinity is an endothermic process.

Explanation:

This is attributed to greater repulsive force which the electron being added experiences from electrons already present than the attraction from the nucleus, thus work must be done to overcome the effect of repulsion. This work involves input of heat energy.

Note:

Because of the same reason, the 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup> etc electron affinity will have a positive sign. H  $\Delta$

### **FACTORS THAT DETERMINE THE VALUE OF 1<sup>st</sup> E.A**

- 1. Nuclear charge.**
- 2. Atomic radius.**
- 3. Shielding/ screening effect of the inner complete shells of electrons.**
- 4. Electronic configuration of the outer shell of an atom.**

Explanation

#### **1. Nuclear charge**

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

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

#### **2. Atomic radius**

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

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

#### **3. Shielding effect of the electrons in the inner shells.**

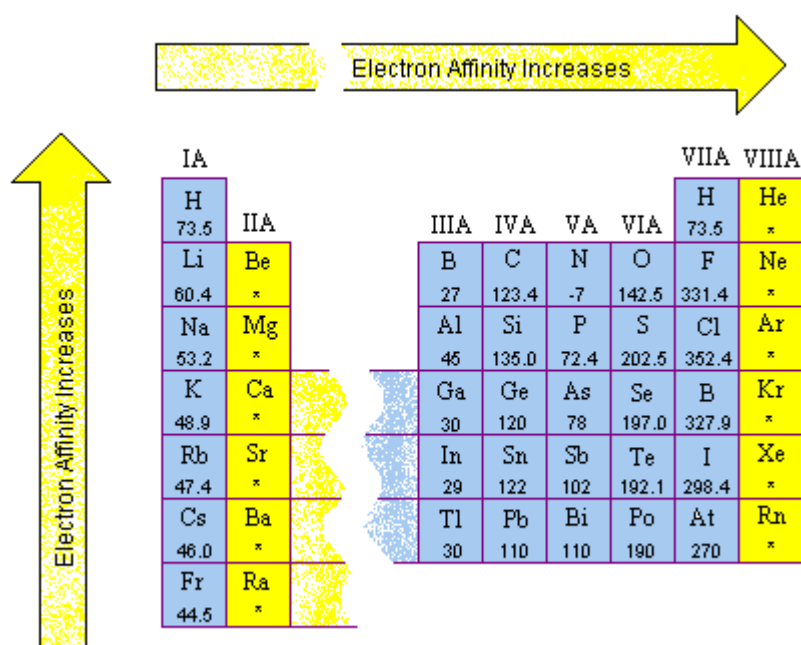
If the screening effect of the electrons in the inner shells is high, electron being added experiences a low attraction from the nucleus leading to a low value of electron affinity.

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

#### 4. Electronic configuration of the outer shell.

If an electron is being added to an atom with a stable outer electronic configuration (i.e. half full or fully filled sub shell), the addition will not occur easily leading to a low value of electron affinity.

Variation of electron affinity



##### i) Across the period.

First electron affinity generally increases on traversing any period in the periodic table.

##### Explanation:

In moving across from one element to the next, electrons are being added to the shells with the same energy as a result the nuclear charge progressively increases while the screening effect of the electrons in the inner shells remains almost constant.

The effective nuclear charge increases leading to increased nuclear attraction for the electron being added and hence an increase in 1<sup>st</sup> E.A.



**ii) Down the group.**

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

Explanation.

In moving down the group from one element to the next, electrons are being added to shells with higher energy levels i.e an extra shell is created.

Both the nuclear charge and shielding effect increase but the increase in shielding effect is more rapid and outweighs that due to nuclear charge as such effective nuclear charge decreases.

Thus electron being added experiences a weaker attraction from the nucleus leading to a decrease in 1<sup>st</sup> E.A

1<sup>st</sup> ELECTRON AFFINITY OF HALOGENS

Element	1 <sup>st</sup> E.A
Fluorine	-328
Chlorine	-349
Bromine	-325
Iodine	-295

Trend

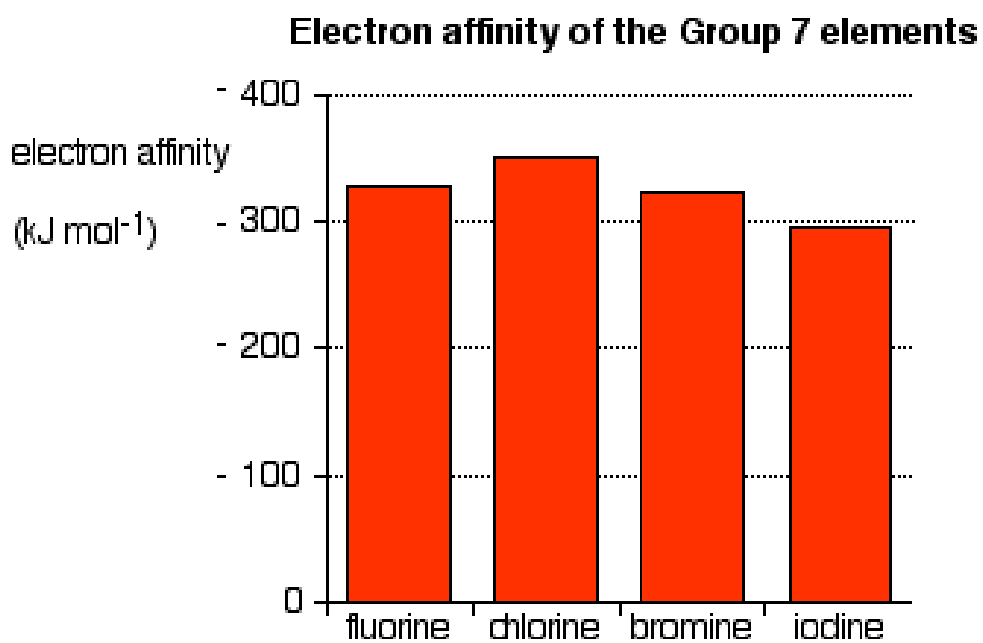
The E.A decreases numerically from Chlorine to Iodine.

As the atomic radius increases down the group, the screening effect of the inner complete shells of electrons increases too.

As such the electron being added experiences a weaker attraction from the nucleus leading to a decrease in 1<sup>st</sup> E.A.

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

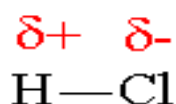
This is due to very small atomic radius of fluorine atom, the 7 electrons in the outermost shell are much closer to each other that they repel each other strongly hence the electron being added experiences a great repulsive force from the electrons already present.



# Electronegativity

**"the power of an atom in a molecule to attract electrons to itself".**

- Linus Pauling



Chlorine is more electronegative than hydrogen. The pair of electrons in the H-Cl bond are pulled toward the Cl giving it a partial negative (-) charge. The H has less electron density and has a partial positive (+) charge. The symbol delta ( $\delta$ ) indicates a partial charge.

## Electronegativity:

is the tendency of an atom in a covalent bond to attract/pull the bonding electrons more towards itself thereby creating partial charges.

## FACTORS THAT DETERMINE ELECTRONEGATIVITY VALUES

- 1. Nuclear charge.**
- 2. Atomic radius.**
- 3. Screening effect of inner electrons.**

### Explanation

1. Nuclear charge.

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

If the nuclear charge is low, the attraction for the bonding electrons will be weaker leading to a low electronegativity value.

## 2. Atomic radius.

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

If the atomic radius is large, the bonding electrons are far from the nucleus and as such experience a weak attraction from the nucleus leading to a low electronegativity value.

## 3. Shielding effect of the electrons in the inner shells.

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

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

## VARIATION IN ELECTRONEGATIVITY

Period 3:

Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

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

### **Explanation:**

As one traverses a period from one element to the next , additional electron is added to shells with the same energy.

As such the nuclear charge increases progressively while the screening effect of the inner complete shells of electrons remains almost unchanged.

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

b) Down the group electronegativity generally decreases .

Group7

Element	Electronegativity
F	4.0
Cl	3.0
Br	2.8
I	2.5

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

The effective nuclear charge decreases as such the attraction for the electrons in the covalent bond decreases leading to a decrease in electronegativity.

## Electronegativity Trends in Periodic Table

	1A	→																8A
1	H	2A	8B										3A	4A	5A	6A	7A	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg	3B	4B	5B	6B	7B	8B		1B	2B	Al	Si	P	S	Cl	Ar	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Ha	Sg	Ns	Hs	Mt									
Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

Electronegativity increases from bottom to top in a column.  
Electronegativity increases from left to right across a group.

## ELECTROPOSITIVITY

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

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

## FACTORS THAT AFFECT ELECTROPOSITIVITY

1. Atomic Radius
2. Nuclear Charge
3. Shielding effect of the inner complete shells.
4. Electronic configuration.

Explanation:

## **1. Atomic radius**

If the radius of an atom is small, the outer most electrons are nearer to the nucleus and experience a high nuclear attraction. Its then not easy for an atom to lose electrons leading to a decrease in electro positivity.

If the radius of an atom is large, the outer most electrons are far from the nucleus and experience a weak nuclear attraction and as a result they can easily be lost leading to an increase in electro positivity.

## **2. Nuclear charge**

When the nuclear charge is high, the electrons in the outer shell are attracted more strongly as such removing an electron is difficult leading to a decrease in electro positivity.

When the nuclear charge is low, the electrons in the outer most shell are attracted less strongly as such removing an electron is relatively easy leading to an increase in electro positivity.

## **3. Shielding effect of inner complete shells**

When the shielding effect of the inner complete shells is high, the effective nuclear charge decreases as such electrons in the outer most shell are less attracted to the nucleus. Removal of these electrons is easy leading to increase in electro- positivity.

When the screening effect is low, the effective nuclear charge increases as such electrons in the outer most shell are attracted more strongly to the nucleus. Removal of these electrons is difficult leading to a decrease in electro positivity.

## **4. Electronic configuration**

If the outer most shell is fully or half filled, it is thermodynamically stable and an electron can not easily be lost leading to a decrease in electro positivity.

However, when electron pairing begins in one of the orbitals, the paired electrons experience mutual repulsion between them thus can easily be lost leading to an increase in electro positivity.

## **Variation of electro positivity**

**a) Electro positivity increases in moving down the group in the periodic table.**

Explanation:

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

This decreases the effective nuclear charge as a result the attraction for the outer most electrons reduces hence they can easily be lost leading to an increase in electro positivity.

**b) Electro positivity decreases in moving across the period**

Explanation

Across the period, the nuclear charge progressively increases while the screening effect of the inner complete shells remains almost unaltered from one element to the next as additional electron is added to shells with the same energy .

This increases the effective nuclear charge as such electrons in the outer most shell are attracted more strongly leading to increase in electro positivity.

## **MELTING POINT**

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

### **FACTORS THAT DETERMINE MELTING POINT**

**a) metals**

The melting points of metals depend on the following factors:

1. The number of electrons available for metallic bonding(delocalized electrons).



The greater the number of electrons contributed for metallic bonding the stronger the bond and the higher is the melting point.

## 2. The atomic radius.

When the radius of a metallic atom is small, the bonding electrons are attracted more strongly by the nucleus making the inter-atomic (element-element) bond length to be shorter and stronger thus high melting point.

When the radius of a metallic atom is large, the metallic bonding electrons are weakly attracted by the nucleus as a result the element-element bond becomes longer and weaker leading to a low melting point.

## 3. The crystal structure of the element.

### **b) Non-metals(molecular substances)**

Melting points of non-metals depend on:

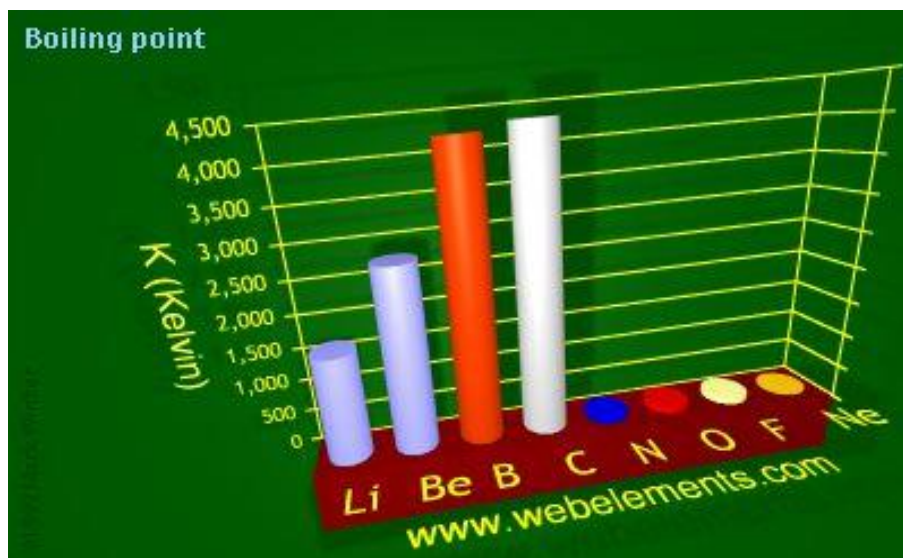
- Molecular mass
- Shape of molecules
- Type of intermolecular forces of attraction.

Trends in melting points/boiling points across period 2

(Li, Be, B, C, N, O, F, Ne)

**Observation:**

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



### Explanation

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

- Increase in number of electrons available for metallic bonding.

(1 for Li, 2 for Be, 3 for B & 4 for C)

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

- Decrease in atomic radius from Li to C.

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

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

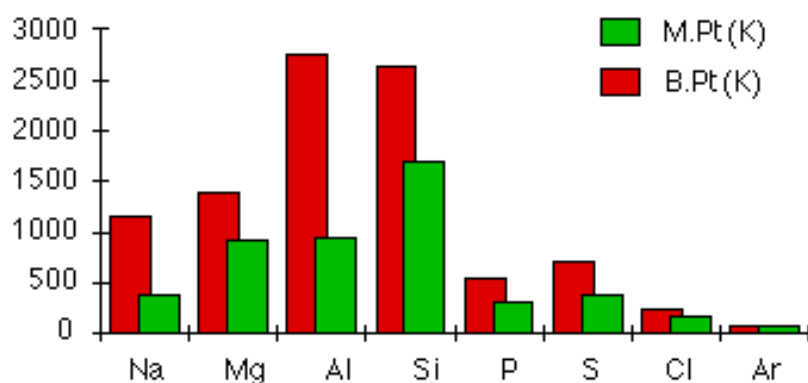
Li has a body centred cubic (b.c.c) structure which has its atoms less efficiently packed than Be with hexagonal closed packed (h.c.p).

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

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

### TRENDS IN MELTING POINTS ACROSS PERIOD 3

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



The melting points increase from Na to Si and drops abruptly for the non metallic elements phosphorus to argon.

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

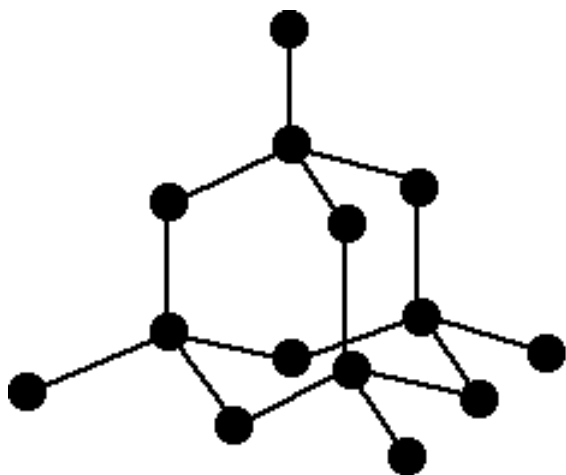
The number of electrons which each atom can contribute to the metallic bonding increases.

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

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

Silicon has the highest melting and boiling points because it has a giant covalent structure.

Here strong covalent bonds have to be broken before it melts or boils.

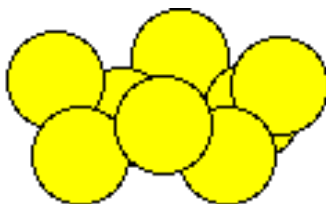


Phosphorus, sulphur, chlorine and argon have simple molecular structures held by weak van der Waals forces of attractions. Thus their melting points are much lower.

The melting and boiling points of non metals are governed entirely by the sizes of the molecules.



a P<sub>4</sub> molecule



an S<sub>8</sub> molecule



a Cl<sub>2</sub> molecule



an Ar molecule

(not drawn to scale)

### Phosphorus

Phosphorus contains smaller P<sub>4</sub> molecules. To melt phosphorus you don't have to break any covalent bonds - just the much weaker van der Waals forces between the molecules.

### Sulphur

Sulphur consists of larger S<sub>8</sub> rings of atoms. The molecules are bigger than phosphorus molecules, and so the van der Waals forces of attractions will be stronger, leading to a higher melting and boiling point.

### Chlorine

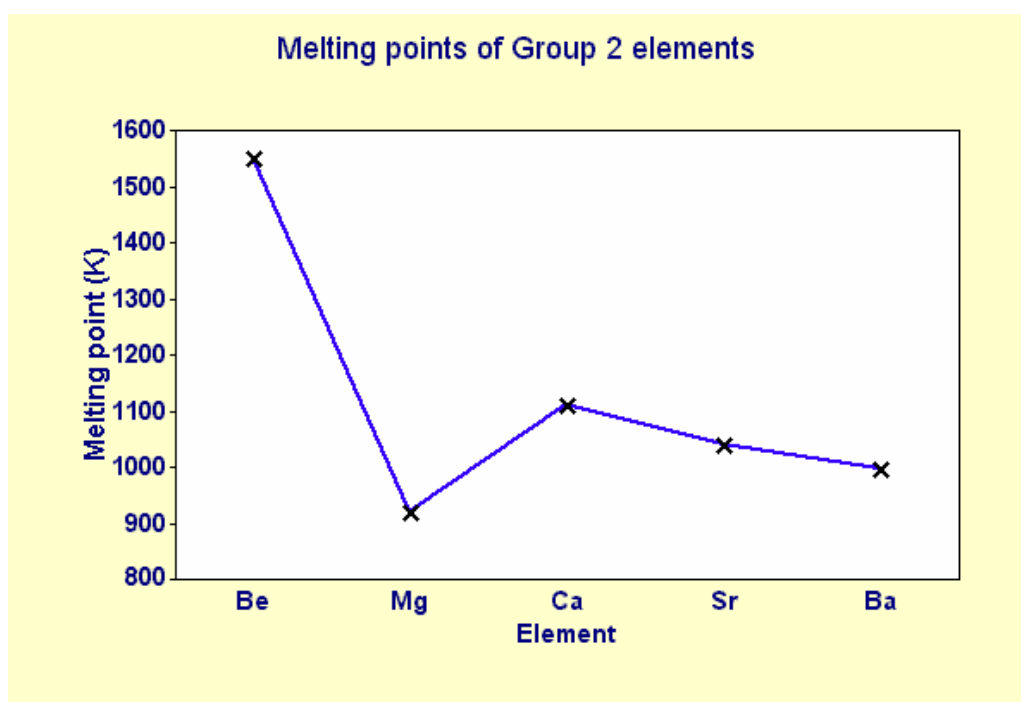
Chlorine, Cl<sub>2</sub>, is a much smaller molecule with comparatively weak van der Waals forces of

attractions, and so chlorine will have a lower melting and boiling point than sulphur or phosphorus.

#### Trend in melting points of Group 2 elements

The melting and boiling points of group 2 metals are higher than those of corresponding group 1 elements.

Graph of physical data



Explanation of this trend

Melting points generally **decrease** going **down** Group 2.

- The Group 2 elements are all metals with metallic bonding. In metallic bonding, metal cations in a metal lattice are attracted to delocalized electrons.
- Therefore going down Group 2:
  - the number of delocalized electrons remains the same.
  - the charge on each metal cation stays the same at +2, but..

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

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

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

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

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

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

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

## 2. SOLUBILITY OF IONIC SALTS

Solubility of ionic salts in water is governed by two energy terms:

- I. *Lattice energy*,
- II. *Hydration (solvation) energy*.

### **Lattice energy**

is the amount of energy required to break 1 mole of an ionic salt into its constituent gaseous ions at standard conditions.



Or

### **Lattice energy**

is the amount of energy released when 1 mole of an ionic salt is formed from its constituent gaseous ions at standard conditions.



## Hydration energy

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



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

NB:

1. Each ion has its own hydration energy.



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

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

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

- it is a polar solvent,
- has a high dielectric constant.
- has a large dipole moment, so that ion-dipole interaction is high.

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

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

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

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

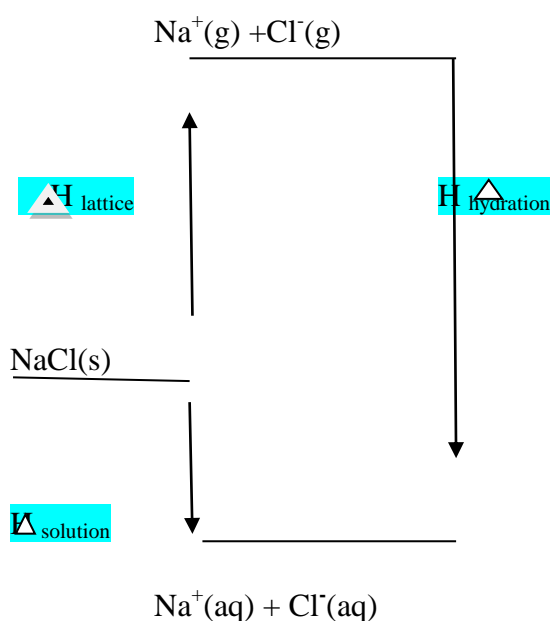


Figure shows Born-Haber cycle for solubility of NaCl.

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

NB:

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

**Qn1.**

The lattice and hydration energies of  $\text{MgCl}_2$  are -2644 kJ/mole and -2653 kJ/mole respectively.

i) Draw an energy diagram/ *Born-Haber cycle* for the solubility of  $\text{MgCl}_2$  and indicate the energy changes that occur.



ii) Calculate the enthalpy of solution of the salt.

### Qn2.

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

ii) The enthalpy of solution and lattice energy of potassium iodide are +21kJ/mol and -642kJ/mol respectively. Calculate the hydration energy for potassium iodide.

#### Factors that affect lattice energy

- Ionic charge ( charge on the ion e.g  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ )
- Ionic radius ( distance between the ions)
- Crystal structure of a compound.

#### Explanation

Lattice energy is directly proportional to the ionic charge.

- ✓ If ionic charge is large, the electrostatic forces of attraction between the opposite charges is stronger leading to a high lattice energy.
- ✓ If ionic charge is small, the electrostatic forces of attraction between the opposite charges is weaker leading to a low lattice energy.

Lattice energy is inversely proportional to ionic radius.

- If ionic radius is large, the electrostatic forces of attraction between the opposite charges is weaker leading to a low lattice energy.
- On the other hand if the distance between the ions is small, the electrostatic forces of attraction between the opposite charges is greater leading to a high lattice energy.

#### **Variation in Lattice & Hydration energies**

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

### **Explanation**

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

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

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

### **Explanation.**

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

## **3. DIAGONAL RELATIONSHIP**

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

This is particularly noticeable with the following pairs.

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

### **Causes of diagonal relationship:**

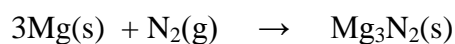
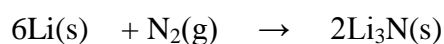
- I. Similar electro negativities,
- II. Similar atomic & ionic radius ,
- III. Similar hydration energies,
- IV. Similar electrode potentials,

V. Similar charge densities & similar polarizing powers,

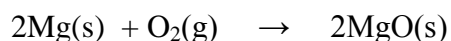
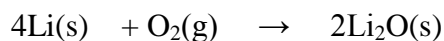
VI. Similar electropositivities.

***Resemblance between Li & Mg***

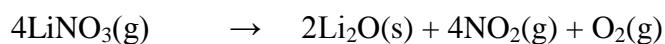
(1) Both react directly with nitrogen to form nitrides on heating.



(2) Both react with oxygen gas to form normal oxides only.



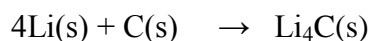
(3) Both their nitrates decompose on heating to form normal oxide, nitrogen dioxide and oxygen gas.



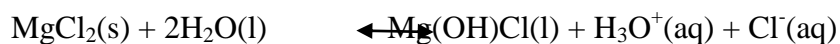
(4) both form carbonates that decompose on heating.



(5) Both react with carbon when heated to form ionic carbide.



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

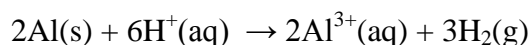
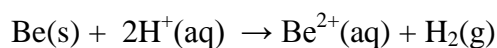
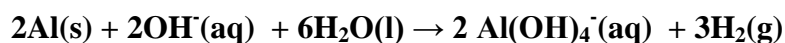
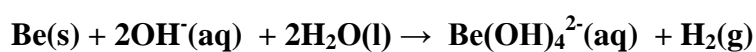


The oxonium ions produced makes the resultant solution acidic.

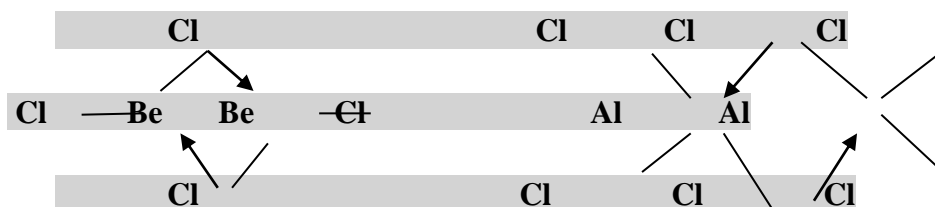
***Resemblance between Beryllium and aluminium:***

(1) Both elements are passive to concentrated nitric acid.

(2) Both react with conc. alkalis (to form complex) and mineral acids. (amphoteric metals)

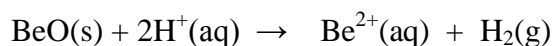
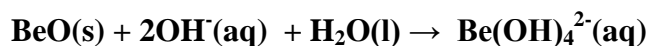


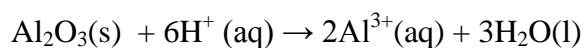
(3) Both elements form chlorides which are partly covalent and exist as dimmers.



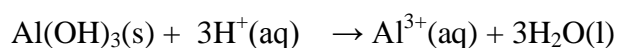
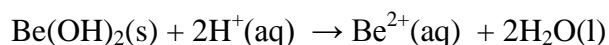
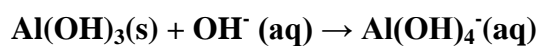
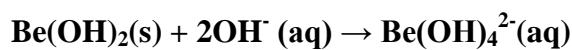
(4) Their oxides are amphoteric as are their hydroxides.

Oxides

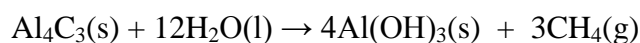
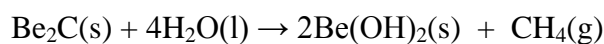




### Hydroxides



(5) Both their carbides hydrolyze in water to form methane gas.



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

- ✚ Similar electro negativities,
- ✚ similar electrode potentials,
- ✚ similar hydration energies,
- ✚ similar ionization energies.
- ✚ their ions have similar charge densities and polarizing powers

### **GROUP 1 ELEMENTS(Alkali Metals)**

(Li, Na, K, Rb, Cs)

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

They have one valence electron with outer most shell electronic configuration of  $ns^1$ .

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

They have the largest atomic radius and lowest ionization energy in any period.

They are highly electropositive and the most reactive metals.

### **GROUP 2 ELEMENTS(Alkaline Earth Metals)**

(Be, Mg, Ca, Sr, Ba)

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

The general electronic configuration of their outer shell is  $ns^2$

They have a smaller atomic radii than corresponding group 1 metals.

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

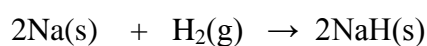
They have a higher 1<sup>st</sup> ionization energies than corresponding elements in group 1.

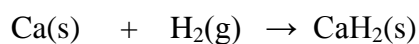
They are less electropositive, less reactive and form more covalent compounds than group 1.

### **CHEMICAL PROPERTIES OF GROUP 1& 2 METALS**

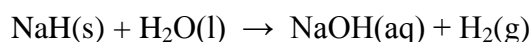
1. Reaction with Hydrogen.

The more electropositive metals of group 1 & 2 react with hydrogen to form ionic hydride except Be and Mg which form covalent hydride.





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



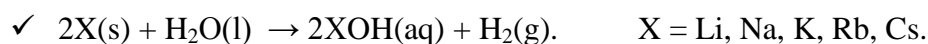
## 2. Reaction with Water.

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

### Explanation

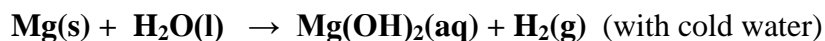
These metals form positive ions in the course of their reaction. Group I lose one electron while group II lose two electrons. Therefore less energy is required to remove one electron than two from the outer most shell as such group I metals react faster with water than corresponding metals of group II.

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

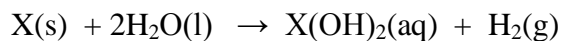


✓ Be does not react with water.

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



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



X= Ca, Sr,& Ba.

NB

The hydroxides of Be & Mg have low solubility in water. However the solubility of hydroxides increase from Ca(OH)<sub>2</sub> through Sr(OH)<sub>2</sub> to Ba(OH)<sub>2</sub> .

### Explanation

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

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

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

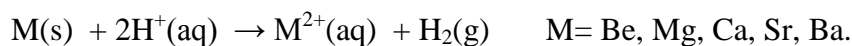
*See table below.*

Hydroxide	Solubility per 100g of water at 25 <sup>0</sup> c
Be(OH) <sub>2</sub>	0.00
Mg(OH) <sub>2</sub>	0.01
Ca(OH) <sub>2</sub>	0.15
Sr(OH) <sub>2</sub>	0.89
Ba(OH) <sub>2</sub>	3.32

### 3. Reaction with Acid.

#### *i) Dilute and concentrated hydrochloric acid*

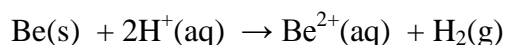
They react similarly with group 2 metals to form corresponding salt and liberating hydrogen gas.



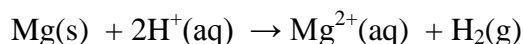


**ii) Dilute sulphuric acid.**

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



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

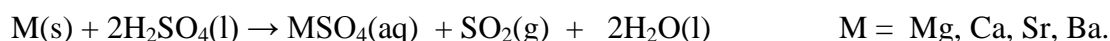


Ca, Sr & Ba react to form a sparingly soluble sulphate which renders the reaction passive.

**iii) Conc. sulphuric acid**

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

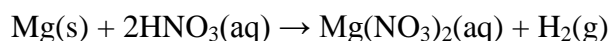
However other members of the group react with conc. sulphuric acid to form salt, sulphur dioxide and water.



**iv) Nitric acid.**

Be does not react with nitric acid at all conditions.

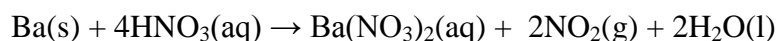
Mg reacts with dilute nitric acid to form salt and hydrogen gas.



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



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



**4. Reaction with Oxygen.**

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

- ❖ Normal oxide ( $\text{O}^{2-}$ )

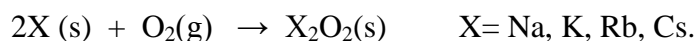
❖ Peroxide ( $\text{O}_2^{2-}$ )

❖ Superoxide ( $\text{O}_2^-$ )

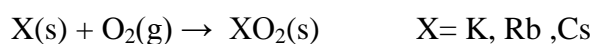
All group 1 metals form normal oxide with oxygen.



Elements Na to Cs in addition form peroxides of the type  $\text{X}_2\text{O}_2$



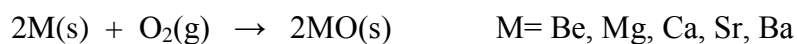
Elements K to Cs in addition form superoxide.



NB:

Li can not form higher oxides due to the fact that  $\text{Li}^+$  is very small, with high charge density & high polarizing power. Thus the larger oxides can not be accommodated around it otherwise the compound would be highly covalent & unstable.

All group 2 metals when heated form normal oxide in oxygen.



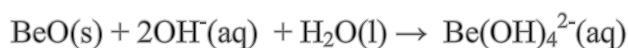
The more electropositive metals form peroxides e.g Sr & Ba.

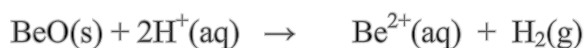


NB:

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

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

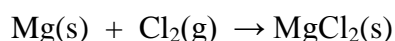
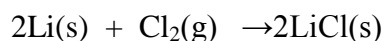




The other oxides are ionic and basic in nature.

#### (5) Reaction with halogens.

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



### COMPOUNDS OF GROUP 1 & 2

1) Compounds of group(ii) tend to be less ionic than those of group(i).

#### **Explanation:**

- ✓ The cations of group 2 have smaller ionic radius than corresponding group 1.
- ✓ Group 2 cations are doubly charged while those of group 1 are singly charged.
- ✓ Therefore cations of group 2 have higher charge density and more polarizing power than corresponding group 1. As such compounds of group 2 are less ionic than corresponding group 1 compounds. e.g.  $\text{MgCl}_2$  and  $\text{NaCl}$ .

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

#### **Explanation**

- The cations of group 2 have smaller ionic radius than corresponding group 1.
- Group 2 cations are doubly charged while those of group 1 are singly charged.
- Therefore the lattice energy of group 2 salts are much higher than those of corresponding group 1 salts.

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

### **SULPHATES OF GROUP 1 & 2**

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

Sulphates of group 2 are white solids and sparingly soluble in water. Their solubility decrease down the group.

Sulphate	Solubility per 100g of water at 25 <sup>0</sup> c
BeSO <sub>4</sub>	43
MgSO <sub>4</sub>	36
CaSO <sub>4</sub>	0.20
SrSO <sub>4</sub>	0.011
BaSO <sub>4</sub>	0.0024

#### **Explanation.**

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

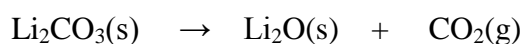
Therefore the decrease in solubility of the sulphates down the group is attributed to the fact that the hydration energy of the sulphates decreases more rapidly than the lattice energy down the group.

**NB**

Solubility of the nitrates , carbonates and chromates are similar to those of the sulphates.

### CARBONATES OF GROUP 1 & 2

The carbonates of group1 metals are white solids ,readily dissolve in water and are stable to heat except lithium carbonate which decomposes on heating.

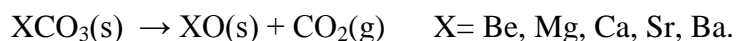


#### Explanation

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

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

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



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

Carbonate	Decomposition temp. $^{\circ}\text{C}$
$\text{BeCO}_3$	100
$\text{MgCO}_3$	350
$\text{CaCO}_3$	900
$\text{SrCO}_3$	1290
$\text{BaCO}_3$	1350

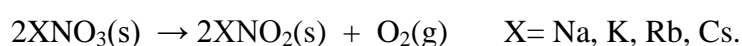
### Explanation

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

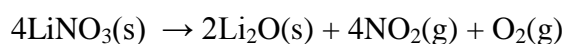
Since an oxide is smaller than a carbonate, the decomposition of metal carbonates become less energetically favourable down the group.

### **NITRATES OF GROUP 1 & 2**

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



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



### Explanation

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

As such the smaller oxide ion ( $O^{2-}$ ) with a similar charged density approaches the  $Li^+$  ion more closely with least polarization thus forming a stable oxide.

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

### **COMPLEX FORMATION BY GROUP 2 CATIONS**

Complex ion formation is favoured by:

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

E.g  $\text{Be}(\text{OH})_4^-$ ,  $\text{Be}(\text{H}_2\text{O})_4^{2+}$

Beryllium cation forms complex easily due to its very small ionic radius & high charge density.

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

**Reactions in which Be resembles other group 2 elements include:**

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

**Reactions in which Be differs from other group 2 metals include:**

- Be reacts with conc. alkalis but others don't.
- $\text{BeO}$  oxide is amphoteric, reacts with both acid and alkalis. Other oxides of the group are basic in nature.
- Be carbide reacts with water to form methane. Other members of the group don't.
- Be forms chloride which is partly covalent and exist as dimmers. Other members form ionic chlorides.
- Be forms only one type of oxide, the monoxide. Other members form more than one type of oxide.

Qn.

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

i) Calculate the empirical formula of Z.

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

iii) Write the structural formula of Z.

**Qn.**

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

i) Calculate the empirical formula of X.

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

iii) Write the structural formula of X.

**Qn.**

When 0.13g of a chloride of iron was vaporized at 600k and 1 atmosphere pressure, 20cm<sup>3</sup> of vapor was formed.

i) Calculate the relative mass of iron chloride.

ii) Determine the molecular formula of the iron chloride.

iii) Write the structural formula of the iron chloride.

**Qn.**

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

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

**Qn.**

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

i) warm dilute sulphuric acid.

ii) warm conc. sodium hydroxide.

#### 4. ALUMINIUM



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

Impurities found in the ore are:

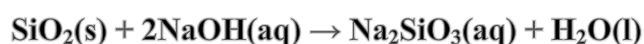
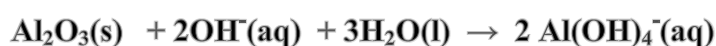
- Silica,  $\text{SiO}_2$
- iron(iii) oxide,  $\text{Fe}_2\text{O}_3$

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

### **Purification of bauxite**

The ore is roasted and then crushed to powder.

Conc. sodium hydroxide is added to dissolve the amphoteric oxide,  $\text{Al}_2\text{O}_3$  and the acidic oxide  $\text{SiO}_2$



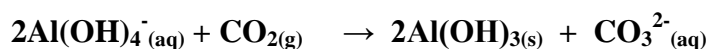
The impurity,  $\text{Fe}_2\text{O}_3$ , is eliminated by filtering off.

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

- i) by adding a little prepared aluminium hydroxide to the filtrate.



- ii) by bubbling  $\text{CO}_2$  gas through the filtrate to remove the excess  $\text{OH}^-$  ions.



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

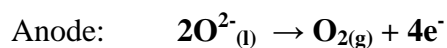
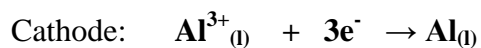


### **Extraction of Aluminium ( By electrolysis of the fused ore)**

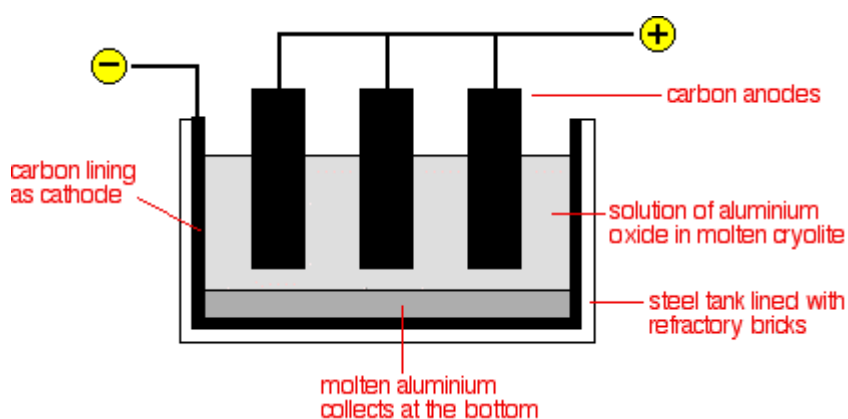
The pure oxide is 1<sup>st</sup> dissolved in molten cryolite (sodium aluminium fluoride -  $\text{Na}_3\text{AlF}_6$ ) to lower its melting point.

The melt is then electrolyzed at a temperature between 800-900 °C at a high current density between graphite electrodes.

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



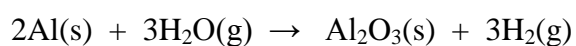
*The electrolysis cell*



### Reactions of aluminium

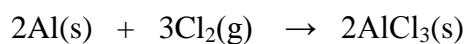
#### a) Reaction with water.

Aluminium reacts slowly with steam to form the oxide and hydrogen gas.



#### b) Reaction with chlorine.

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



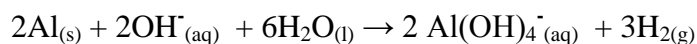
### Explanation

Aluminium forms a smaller cation with high charge density & high polarizing power. It distorts the electron cloud of surrounding anions. The larger the anion, the greater the extent of polarization. Therefore the large chloride ion is polarized greatly and as such a covalent character is induced.

The chloride forms dimer,  $\text{Al}_2\text{Cl}_6$ , at high temperature with a chloride bridge structure. Aluminium bromide & iodide have similar structures.

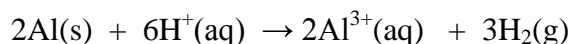
### c) **Reaction with solution of alkalis (NaOH & KOH).**

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



### d) **Reaction with acids.**

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



With hot conc.  $\text{H}_2\text{SO}_4$ , aluminium forms salt, sulphurdioxide gas and water.



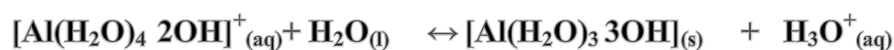
Aluminium does not react with dilute nitric acid. The metal is rendered passive due to the formation of an impervious layer of oxide.

### **The acidity of the hexa-aqua ions**

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

The resultant solution is acidic due to hydrolysis reactions:





**Over all equation:**

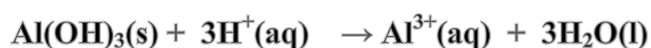
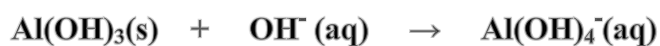
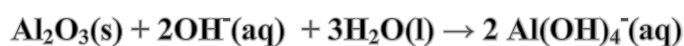


**white ppt**

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

If sodium carbonate solution is bubbled through aqueous solution of aluminium salts, bubbles of a colorless gas that turns lime water milky is formed.

The oxide and hydroxide of aluminium are amphoteric. They react with both conc. alkalis and dilute acids.



**Some uses of aluminium include:**

<b>Aluminium is used for:</b>	<b>Because</b>
1. Aircraft	light, strong, resists corrosion
2. other transport such as ships' superstructures, container vehicle bodies, tube trains	light, strong, resists corrosion

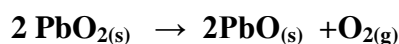
3. overhead power cables .	light, resists corrosion, good conductor of electricity
4. Saucepans	light, resists corrosion, good appearance, good conductor of heat

## 5. GROUP (IV) ELEMENTS

(Carbon, Silicon, Germanium, Tin, and Lead)

- ✓ All group(iv) elements have four electrons in their outermost shell with a general outer configuration of  $ns^2np^2$   
 $n=2$  for C,  $n=3$  for Si,  $n=4$  for Ge,  $n=5$  for Sn  $n=6$  for Pb etc
- ✓ Metallic character increases down the group as the radius of the atoms become larger. Carbon and Silicon are non metals , Germanium is a metalloid ie it exhibits properties characteristics of metals and non metals. While Tin & Lead are weak metals.eg they form amphoteric oxides
- ✓ All elements show an oxidation states of +2 and +4. The +2 oxidation state arise due to the inability of the outer most paired 's' electrons to take part in bond formation. This is called the inert pair effect.
- ✓ The stability of the +2 oxidation state increases down the group from carbon to lead. This is due to increasing metallic character and increasing inert pair effect as the group is descended.eg Carbon and Silicon form extremely unstable compounds in +2 oxidation state.

- ✓ Germanium and tin compounds in +2 oxidation state are predominantly covalent and are readily oxidized i.e. they are powerful reducing agents.
- ✓ Lead invariably forms more stable compounds in +2 oxidation state than +4 oxidation state. Also compounds of lead in +2 oxidation state are ionic in nature. Therefore lead (IV) compounds are unstable, and readily decompose to +2 oxidation state. eg



- ✓ The stability of +4 oxidation state decreases down the group. Carbon, silicon and germanium form more stable compounds in +4 oxidation state than in +2. This could explain why their compounds in +2 oxidation states are good reducing agents.
- ✓ Carbon is the only member of the group whose covalency is restricted to a maximum of +4. This is due to absence of the vacant 'd' orbitals. Other elements have a maximum of +6 due to the availability of vacant d-orbitals which allows them to expand their octet.
- ✓ However, all the elements exhibit a covalency of 4 but compounds of the type  $\text{M}^{4+}$  or  $\text{M}^{4-}$  are rare. This is because the sum of the first four ionization energies or first four electron affinities would be highly endothermic. An ion of the type  $\text{M}^{4+}$  would be very small with high charged density as such would exert high polarizing effect on the surrounding anion thus making the compound formed highly covalent & unstable.

NB:

Carbon, however, being the most electronegative with the smallest atomic radius and least number of electrons is most likely to form compounds of the type  $\text{M}^{4+}$  or  $\text{M}^{4-}$

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

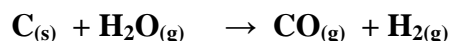
- ✓ Carbon therefore form limitless hydrides, alkanes, alkenes, alkynes etc due to catenation. This unique property of carbon is attributed to the small atomic radius of carbon. The electrons involved in bond formation between two carbon atoms are closer to the nuclei and are strongly held by it thus making bonds very strong and stable. However as you descend the group, atomic radius increases. Therefore electrons between the atoms become more distant from the nuclei making the bond weaker and unstable.
- ✓ The melting points of group(iv) elements decrease as the group is descended. Carbon, however, has a much higher melting point than others. This is because carbon has a giant molecular (Macro-molecular) structure composed of many atoms due to its ability to catenate. It has abnormally high melting point because large number of short and strong carbon –carbon bonds have to be broken before it melts.

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

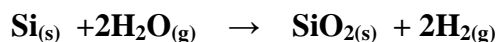
### **CHEMICAL PROPERTIES OF GROUP (IV) ELEMENTS.**

1.Reaction with water.

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

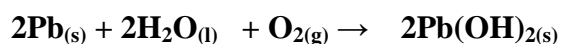


Silicon reacts with steam when heated to form silicon dioxide and hydrogen gas.



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

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



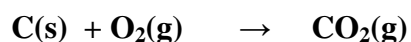
NB

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

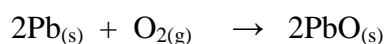
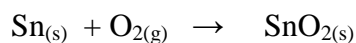
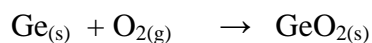
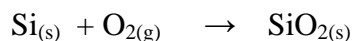
## 2. Reaction with Oxygen (air).

### a) Carbon.

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



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

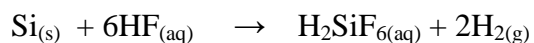


## 3. Reaction with acids.

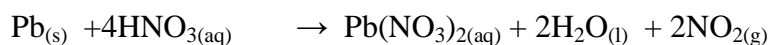
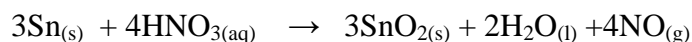
a) Carbon is attacked by all oxidizing acids eg hot conc. Sulphuric acid and hot conc. Nitric acids.



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



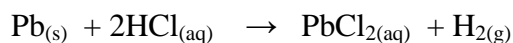
c) Germanium, Tin and Lead are oxidized by hot conc. nitric acid



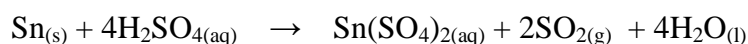


Lead is rendered passive in both cold dilute hydrochloric and sulphuric acids due to formation of insoluble salt of lead(ii) chloride & lead(ii) sulphate respectively.

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



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



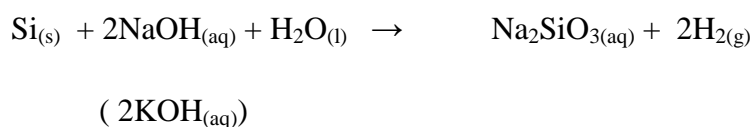
Lead reacts with hot conc. Sulphuric acid to form lead(ii) sulphate, sulphur dioxide and water.



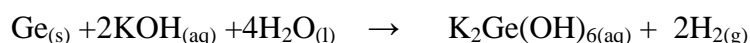
This reaction is similar to Al & Chromium

#### 4. Reaction with Alkalis

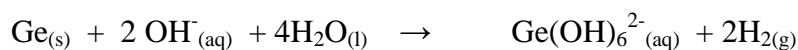
Carbon is resistant to alkalis but silicon dissolves in conc. Solution to form silicate.



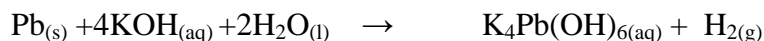
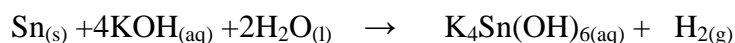
Germanium dissolves in conc. Alkalis to form hexa-hydroxo-germanate (iv)



Ionicallly:



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



## COMPOUNDS OF GROUP(IV) ELEMENTS

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

### THE OXIDES OF GROUP 4

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

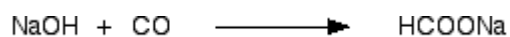
The oxides of the elements at the top of Group 4 are acidic, but acidity of the oxides falls as you go down the Group. Towards the bottom of the Group, the oxides become more basic - although without ever losing their acidic character completely.

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

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

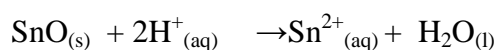
### MONOXIDES

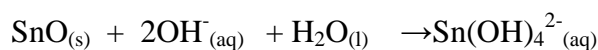
The monoxide of carbon and silicon are usually treated as neutral oxides, but in fact carbon monoxide is very, very slightly acidic. It doesn't react with water, but it will react with hot concentrated sodium hydroxide solution to give a solution of sodium methanoate.



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

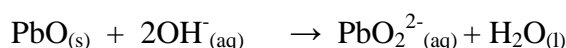
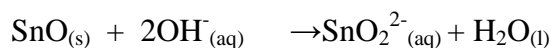
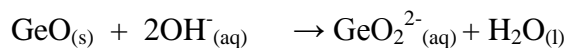
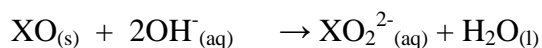
Those of germanium, tin and lead are amphoteric. The amphoteric monoxides ( GeO, SnO and PbO) react with acids to give corresponding salts and alkalis to give germanate(ii), stannate(ii) and plumbate(ii) complex ions.



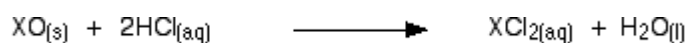


Similar reactions are undergone by GeO & PbO

Alternatively:

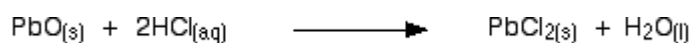


They all react with concentrated hydrochloric acid.



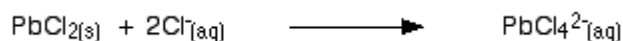
... where X can be Ge and Sn, but unfortunately needs modifying a bit for lead.

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



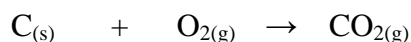
However, using concentrated hydrochloric acid the large excess

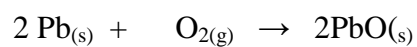
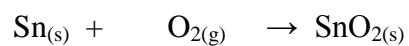
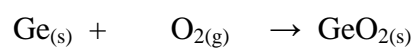
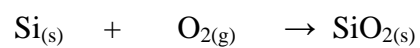
of chloride ions in the concentrated acid react with the lead(II) chloride to produce a yellow soluble complex  $\text{PbCl}_4^{2-}$ .



## DIOXIDES

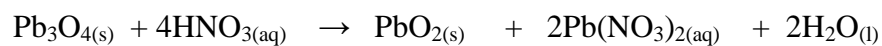
The first four dioxide are prepared by heating the elements in oxygen but a similar process with lead gives lead(ii) oxide.





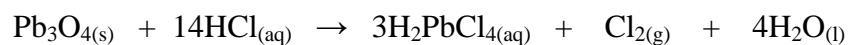
NB

Lead(iv) oxide is made by action of hot dilute nitric acid on red lead,  $\text{Pb}_3\text{O}_4$ .



Brown solid

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

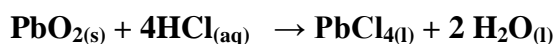


Yellow solution

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

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

Here the acid should be cold and conc.

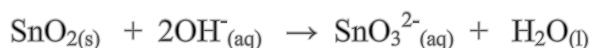


If the reaction is carried out at elevated temperature, lead(IV) oxide reacts with hydrochloric acid to give lead(II) chloride and chlorine gas.



### The acidic nature of the dioxides

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

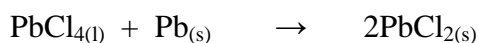


### THE HALIDES OF GROUP 4

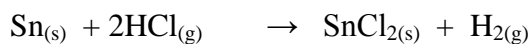
+2 halides

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

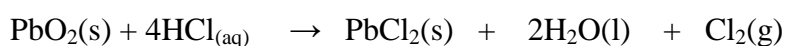




Tin(ii) chloride may be prepared in anhydrous form by passing dry



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

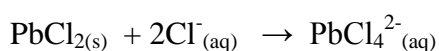


Conditions: hot/ conc. acid,

NB: Lead(ii) chloride is more soluble in concentrated hydrochloric acid than in water. This observation is due to the formation of chloroplumbate(ii) ions.

Lead(ii) chloride has a high lattice energy which is not overcome in hot water. However on heating, the high lattice energy is overcome and there is a change in solubility.

Lead(ii) chloride dissolves in conc. Hydrochloric acid due to form chloroplumbate(ii) ions.



Yellow solution.

#### **+4 halides**

All the elements form tetra chlorides of the type  $\text{XCl}_4$ , which are colorless liquids.

All the tetra chlorides have a tetrahedral shape in which the elements are bonded to four chlorine atoms.

Preparation of the tetra chlorides

#### **CCl<sub>4</sub>**

By reacting chlorine with carbon disulphide .



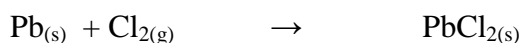
The two liquids are separated by fractional distillation.

### **SiCl<sub>4</sub> , GeCl<sub>4</sub> & SnCl<sub>4</sub>**

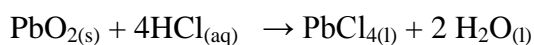
Are prepared by passing a stream of dry chlorine over the heated m



If a stream of chlorine is passed over heated lead, only lead(ii) chl



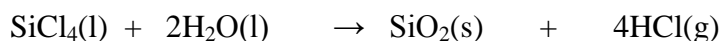
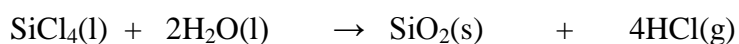
To prepare lead(iv) chloride, use ice cold conc. HCl on lead(iv) oxi



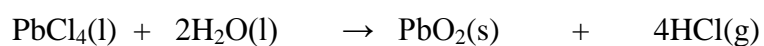
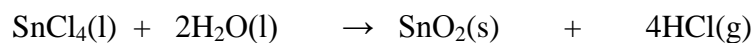
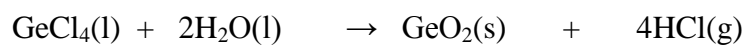
### **Hydrolytic behavior of the tetrachloride**

CCl<sub>4</sub> does not under go hydrolysis in water. This is attributed to absence of the empty d-orbitals.

However, other tetrachlorides under go hydrolysis in water. This is attributed to the presence of the empty d-orbitals thereby allowing the elements to expand their octet and form compounds of more than +4. This empty d-orbitals accept lone pairs of electrons from the water molecule thus facilitating the hydrolysis of the tetra chlorides.



White solid.



Brown solid

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

### Stability of the tetrachloride

The tetrachlorides of carbon, silicon, and germanium are stable to decompose on heating to form di-chlorides.



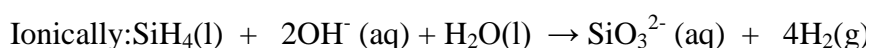
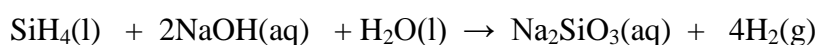
### HYDRIDES OF GROUP 4

$\text{CH}_4$	Methane
$\text{SiH}_4$	Silane
$\text{GeH}_4$	Germane
$\text{SnH}_4$	Stannane
$\text{PbH}_4$	Plumbane



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

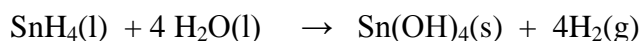
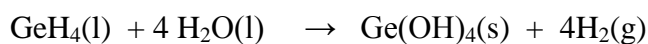
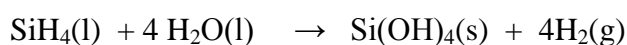
Methane, germane and stannane do not react with sodium hydroxide. Silicon and tin hydrides react with sodium hydroxide to form sodium silicate and hydrogen gas.



Hydrolytic behavior of hydrides of group 4

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

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



**Carbon differs from other group 4 elements in the following ways**

- Its covalency is limited to 4 but others can have a maximum of 6. Due to the absence of vacant d-orbitals in carbon but others have.
- Its unique ability to catenate. Due to its small atomic radius, the bond length between two carbon atoms are closer to the nuclei and are attracted more strongly.
- Its unique ability to form multiple bonds such as:  $-\text{C}=\text{C}-$ ,  $-\text{C}=\text{C}-$ ,  $-\text{C}=\text{C}=\text{C}-$ .
- Its tetrachloride does not hydrolyze in water but tetra chlorides of other group 4 elements hydrolyze. Due to absence of vacant d-orbitals.

➤ Carbon is the only element in group 4 which forms only gas

#### Why carbon differs from other elements in group 4

- Very small atomic radius of carbon atom.
- High electro- negativity of carbon atom.
- Absence of vacant d-orbitals.
- Unable to show the inert pair effect

Qn.

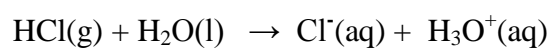
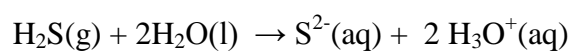
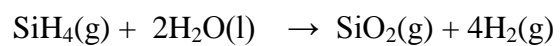
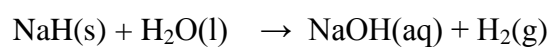
When dilute hydrochloric acid is added to a solution of lead(ii) nitrate, a precipitate is formed, but if the concentrated acid is used, a much less precipitate is formed. Explain this behavior and write ionic equation for the reaction.

#### The Hydrides of period 3

Hydride	Formula
Sodium hydride	NaH
Magnesium hydride	MgH <sub>2</sub>
Aluminium hydride	AlH <sub>3</sub>
Silane	SiH <sub>4</sub>
Phosphine	PH <sub>3</sub>

Hydrogen sulphide	H <sub>2</sub> S
Hydrogen chloride	HCl

**Reaction of hydrides with water**



## 6. GROUP(VII) ELEMENTS

### Physical properties

States at room temperature:

- ✓ Fluorine,  $F_2$ - yellow gas
- ✓ Chlorine  $Cl_2$  - yellow-green gas
- ✓ Bromine  $Br_2$  - red-brown liquid
- ✓ Iodine  $I_2$  - black (dark purple) solid  
- sublimes to a purple vapour.
- ❖ Halogens are highly reactive non-metals. They exist as diatomic molecules  $X_2$  containing a covalent bond. Due to their reactivity the elements do not occur in the free state but are always combined with other elements.
- ❖ All the elements have 7 electrons in their outer most shells with general outer most electronic configuration of  $ns^2np^5$   $n= 2,3,4\&5$
- ❖ They can complete their octet by either gaining an electron to form an ionic bond or sharing electrons with other elements or themselves

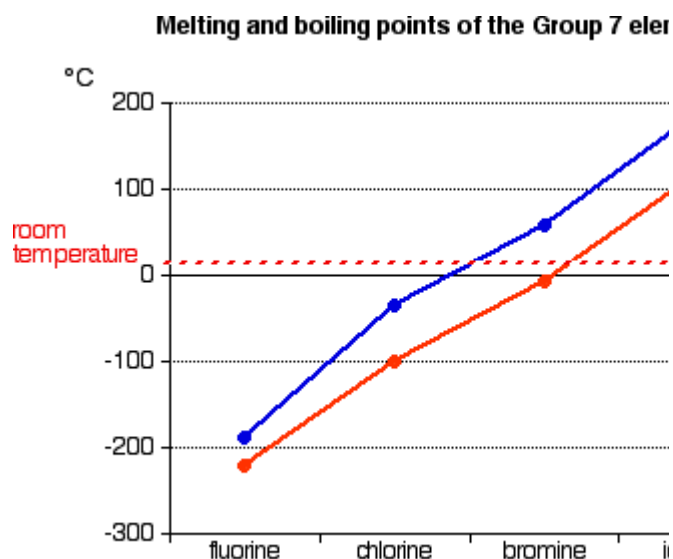
in a covalent bond.

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

### **Explanation**

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

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

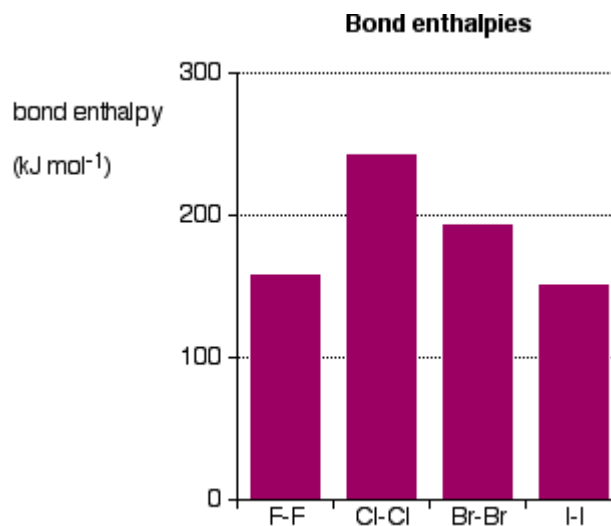


### **Bond dissociation energy**

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

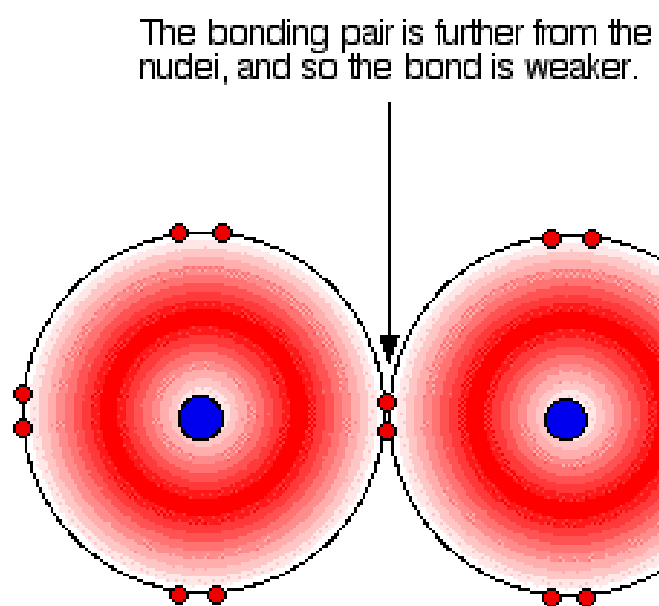
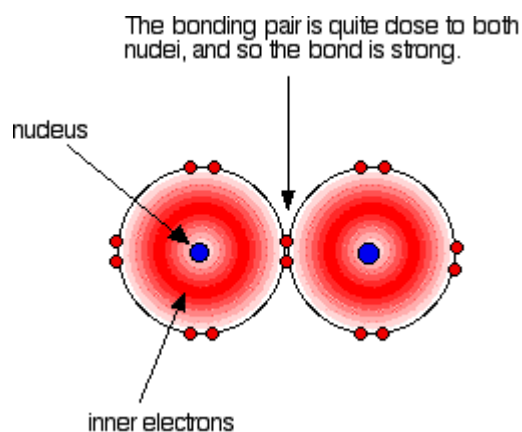
Or it's the energy released when a bond is formed between two atoms.

Bond dissociation energy of the diatomic molecules decreases down the group from chlorine to iodine. However,  $F_2$  has abnormally low bond dissociation energy.



This is due to small atomic radius of fluorine atom, the non bonding p- electrons present in F<sub>2</sub> molecule are closer to one another as such repel @ other strongly thus weakening the F-F bond.

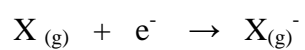
The decrease in B.D.E from Cl<sub>2</sub> to I<sub>2</sub> is attributed to increase in atomic radius as the group is descended, the bonding electrons in the halogen-halogen bond are far from the nuclei of the halogens & are attracted less strongly due to the screening effect of the inner complete shells of electrons thus weakening the bond progressively.



NB: The high reactivity of fluorine may be attributed to its low B.D.E.

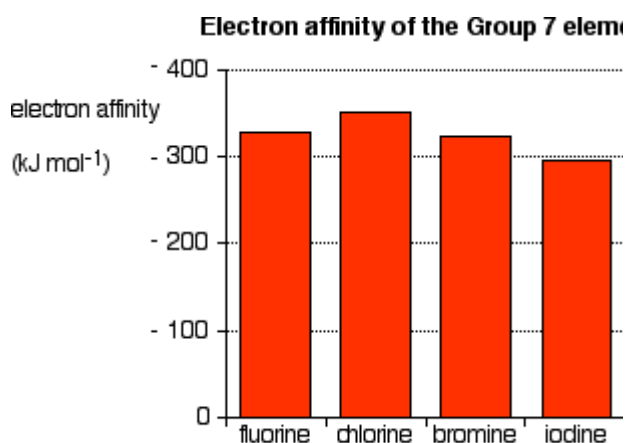
#### Electron affinity of halogens

E.A is the energy change when an extra electron is added to a neutral gaseous atom to form a negatively charged gaseous ion.





The E.A is a more useful concept for the halogens than first ionisation energy because the halogens need only one electron to complete their octet and thereby attain a noble gas like structure.



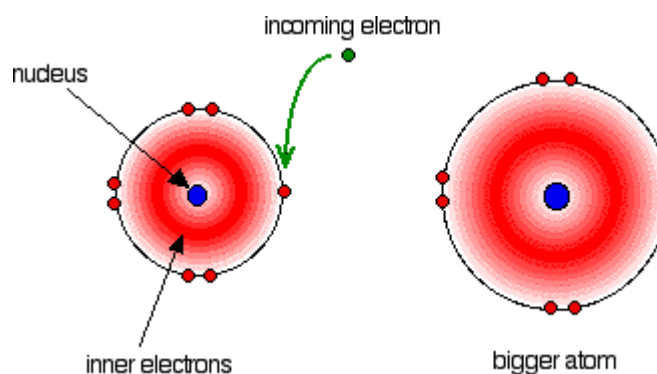
The E.A decreases numerically from Chlorine to Iodine. As the atomic radius increases down the group, the electron being added experiences a greater repulsion from the electrons that are already present than the attraction experienced from the nucleus due to the screening effect of the inner complete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

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

### Explanation

This is due to small atomic radius of fluorine atom, the 7 electrons in the outer most shell are too close to one another therefore the electron being added experiences a greater repulsive force from the electrons already present than the attraction from the nucleus.

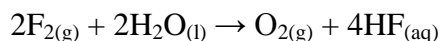
The electron affinity is a measure of the attraction between the incoming electron and the nucleus. The higher the attraction, the higher the electron affinity.



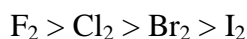
### **Oxidizing properties of halogens**

- ✓ Halogens are very good oxidizing agents with fluorine being the most oxidizing.
- ✓ This is because fluorine is the most electronegative and has the highest positive value for its standard electrode potential. It oxidises water to

oxygen.



- ✓ The standard electrode potential ( $E^\theta$ ) becomes less positive as the group is descended and so oxidising power decreases down the group.



### **Oxidation states of halogens**

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

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

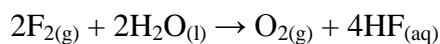
Other elements can show higher oxidation states due to availability of vacant 'd'-orbitals which allows them to expand their octet.

### **Reactions of halogens**

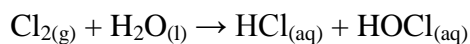
In all their reactions the halogens act as oxidising agents. Hence, their reactivity decreases down the group.

#### **1. Reaction with water**

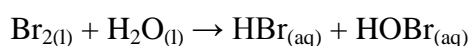
a)  $\text{F}_2$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$  gas in a very exothermic reaction.



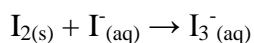
b)  $\text{Cl}_2$  dissolves in  $\text{H}_2\text{O}$  to form 'chlorine water' which is a mixture of two acids. No  $\text{O}_2$  is evolved.



c) Br is only slightly soluble in  $\text{H}_2\text{O}$ .



d)  $\text{I}_2$  is virtually insoluble in  $\text{H}_2\text{O}$ . It is however soluble in KI solution due to the formation of a soluble complex the tri-iodide anion.

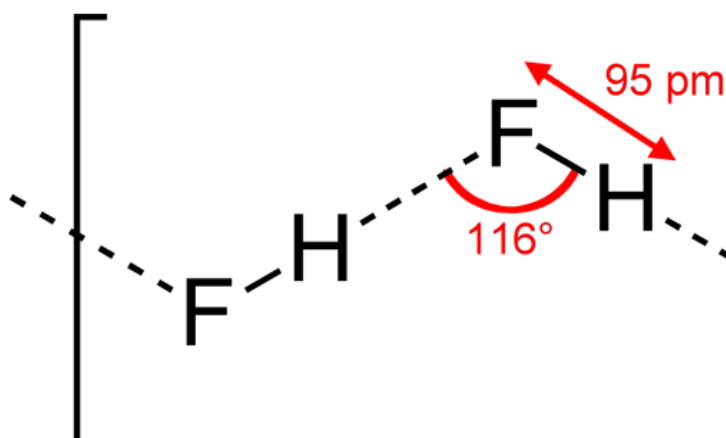


$\text{I}_2$  is sparingly soluble in water because the energy involved in disrupting the weak van der Waals forces in molecular iodine crystal lattice and the hydrogen bonds in water exceeds the energy changes involving the weak attraction between iodine and water molecules.

Note:

All halogens are more soluble in non-polar solvents such as  $\text{CCl}_4$ .  $\text{Cl}_2$  gives a colourless solution.  $\text{Br}_2$  a red solution and  $\text{I}_2$  a violet one.

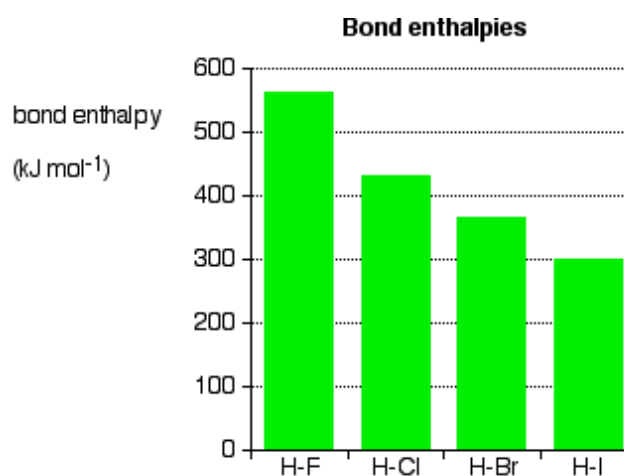
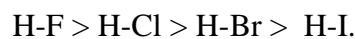
## 2.1



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

- H-F is the weakest acid because the H-F bond is very strong as a result of small atomic radius and high electronegativity of Fluorine atom. It is weakly dissociated in solution releasing fewer  $\text{H}^+$  ions.
- In addition, the presence of hydrogen bonding between HF molecules and water molecules inhibits the ionization of HF in aqueous solution.
- However, as the group is descended, electronegativity decreases whereas atomic radius increases. As such the H- halide bonds become progressively longer and weaker. They dissociate in solution releasing more hydrogen ions.

c) Bond energy/ enthalpy of the hydrides generally decreases in moving from HF to HI ie



*As the halogen atom gets bigger, the bonding pair gets more and more distant from the nucleus. The attraction is less, and the bond gets weaker.*

Fluorine is the most electronegative atom with the smallest atomic radius thus the H-F bond is the most polar. Iodine is the least electronegative with the largest atomic radius as a result the H-I bond is the least polar. The greater the ex-

tent of polarity, the greater the ionic character in the bond and therefore the stronger the bond.

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

- Fluorine is always monovalent, others show higher oxidation state. This because fluorine lacks empty d-orbitals but others have.
- H-F is a liquid while other hydrogen halides are gases at room temperature. This is due to the strong hydrogen bonds between H-F molecules as a result of high electronegativity of fluorine atom.
- Fluorine forms the least acidic hydride whereas the hydrides of other members are fairly more acidic in aqueous solution. This is due to the high strength of the H-F bond.
- Fluorine is the most reactive halogen, due to its low bond dissociation energy and high electronegativity.
- Fluorine forms compounds with more ionic character due to its high electronegativity and charge density of the small F<sup>-</sup> ion.

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

**Why does Fluorine show a difference?**

- Most electronegative in the group.
- Low bond dissociation energy.
- High positive value of standard electrode potential.
- Smallest atomic radius,  $F^-$  ion has very high charge density, high polarising power, high enthalpy of hydration.
- Absence of a vacant d-orbitals.

**Oxy-acids & Oxy-ions**

1.Chlorate(i) acid  $HClO$

(Chloric(i) acid)

2.Chlorate(iii) acid  $HClO_2$

(Chloric(iii) acid)

3. Chlorate(v) acid  $HClO_3$

(Chloric(v) acid)

4. Chlorate(Vii) acid  $HClO_4$

(Chloric(vii) acid)

The acidity of the oxy-anions of



chlorine increases with increase in the number of oxygen atoms attached to chlorine atom. Oxygen being more electronegative than chlorine, withdraws electrons from the O-Cl bond more towards itself.

This weakens the O-H bond in the oxy-acid. The greater the number of oxygen atoms attached the stronger the effect and the stronger the acid.

NB

1. Work out the oxidation state of chlorine in each of oxyacids above .
2. Draw the molecular structure of each oxyacid .

Qn. Compare the reactivity of Fluorine and Chlorine with the following substances( in each case illustrate your answer with equation)

i) Water

## 7. TRANSITION ELEMENTS






























































































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**GENERAL CHARACTERISTICS OF TRANSITION  
ELEMENTS**

**1. High melting and boiling points.**













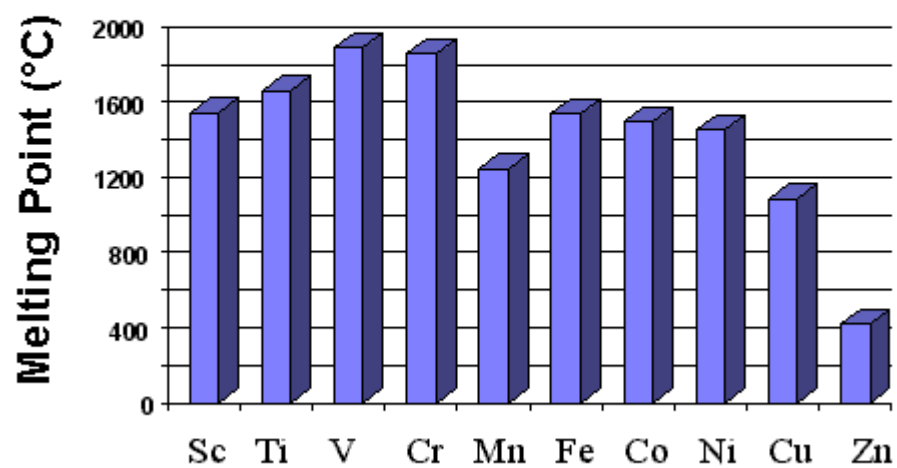








## Melting Points of 4th Period Transition Elements









































































### **Oxidation States of 4th Period Transition Elements**

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

























































































































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## **6. Magnetic Properties**

































## **CHROMIUM**









































































































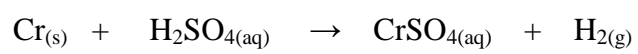
























































































































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**Chromium(iii) oxide, Cr<sub>2</sub>O<sub>3</sub>**



































































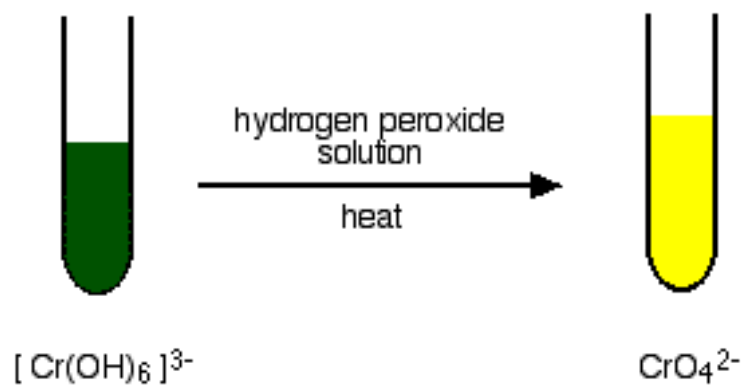
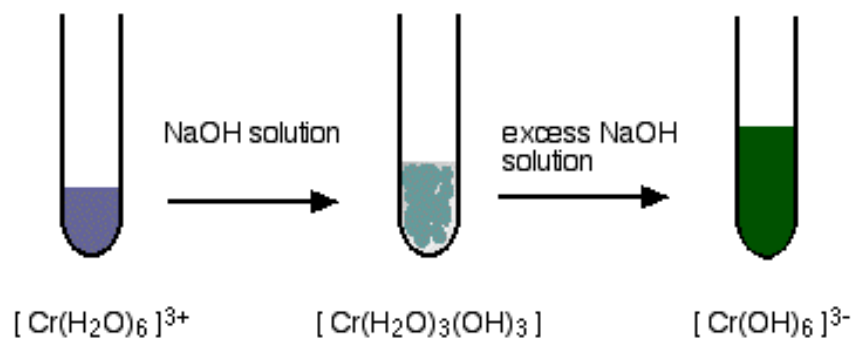
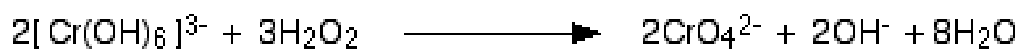




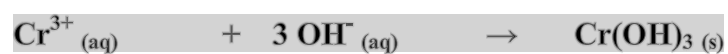








**OR**































































































































































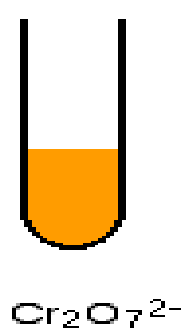
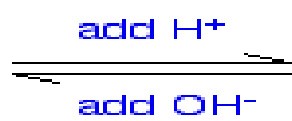
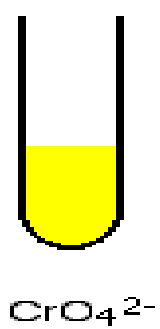












## ALUMS

Alums are double sulphate salts with general formula  $M_2SO_4 \cdot M_2(SO_4)_3 \cdot 24H_2O$

The 1<sup>st</sup> M is a group (I) metal e.g  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $NH_4^+$ ,  $Rb^+$ ,  $Cs^+$  etc

The 2<sup>nd</sup> M is a group (III) metal or a metal bearing a +3 charge e.g  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Mn^{3+}$ ,  $Co^{3+}$  etc

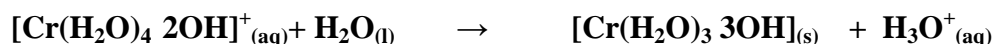
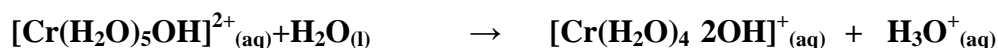
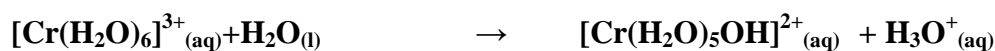
Examples of common alums are:

Chrome alum  $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

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

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

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



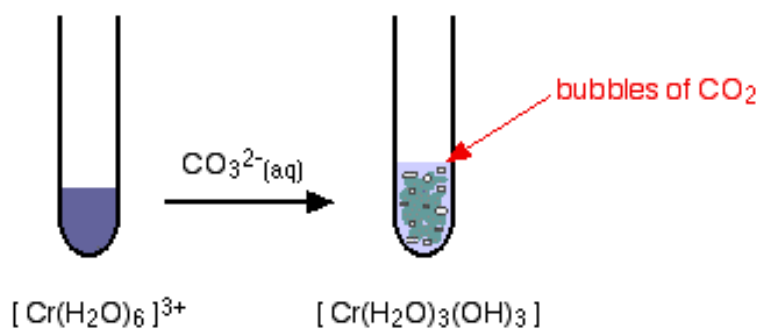
Over all equation:



The accumulation of hydroxonium ions renders the resultant solution acidic.

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



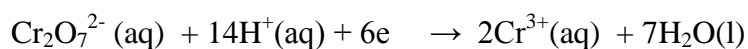
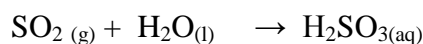


2) Potash alum  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

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

### Preparation of Chrome Alum

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



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

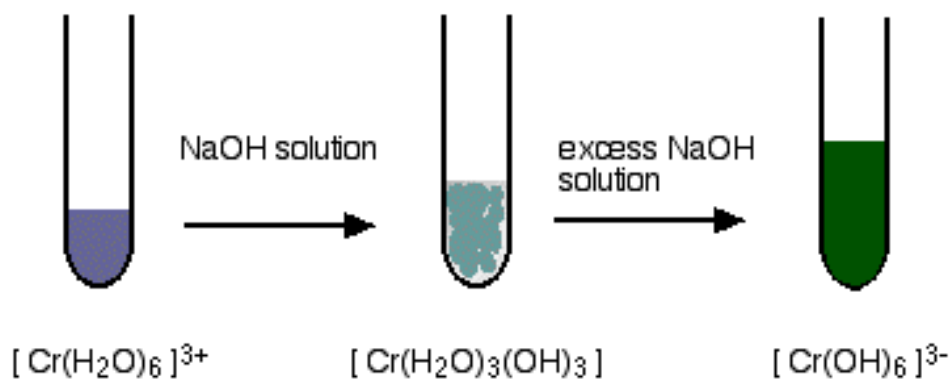
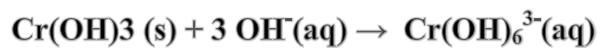
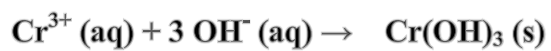
### Test for $\text{Cr}^{3+}$ ions in solution

Use of sodium hydroxide solution:

Observation

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

Equations

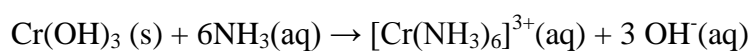
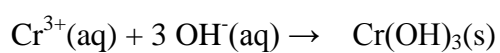


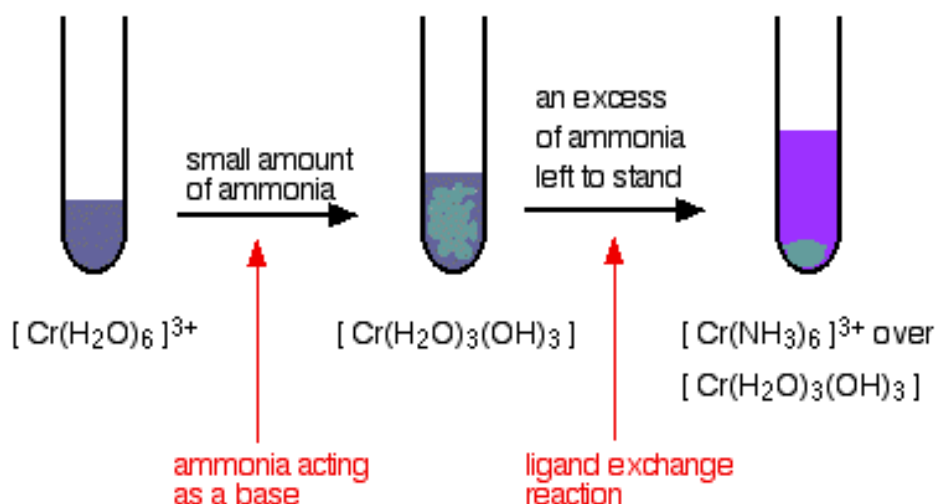
Use of aqueous ammonia solution:

Observation

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

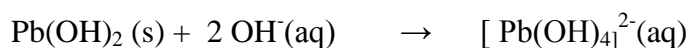
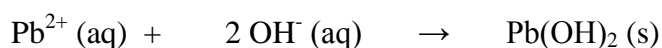
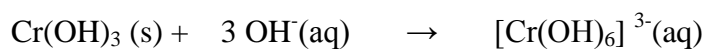
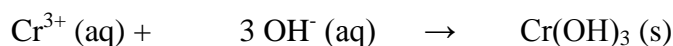
Equations



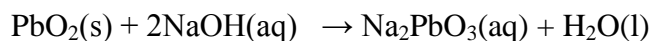
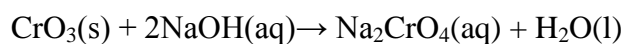


**Suggest similarities in the chemistry of Chromium & Lead**

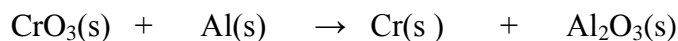
- ✓  $\text{Cr}^{3+}$  and  $\text{Pb}^{2+}$  form complex with sodium hydroxide solution.



- ✓ Both their oxides in higher oxidation states are acidic.



- ✓ Their oxides in higher oxidation states are strong oxidizing agents.



- ✓ They both form compounds with variable oxidation states i.e.

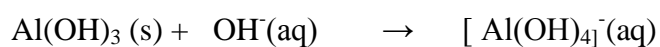
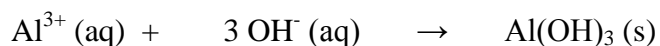
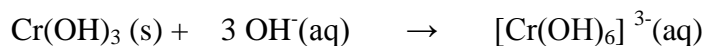
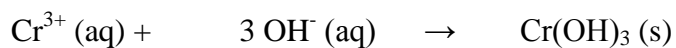
- ✓ Lead: +2 & +4 and Chromium: +2, +3 & +6



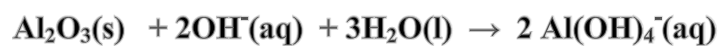
- ✓ Chromium and Lead in higher oxidation states  $\text{Cr}^{6+}$  and  $\text{Pb}^{4+}$  form covalent compounds e.g  $\text{PbCl}_4$  and  $\text{CrCl}_6$

### Similarities 1.1 the chemistry of Chromium & Aluminium

1.  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$  form complex with sodium hydroxide solution.



- 2.



### ZINC

Atomic number is 30.

Its electronic configuration is : $1S^22S^22P^63S^23P^63d^{10}4S^2$

### Ores of Zinc

- Zinc blende : $ZnS$
- Zinc calamine: $ZnCO_3$

### Extraction process from sulphide ore

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

- Concentration

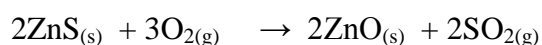
The ore is first crushed and mixed with water and oil (a frothing agent) so as to remove the unwanted earthly materials. The oil wets the sulphide particles and the water wets the impurities.

Air is then blown through the mixture producing a froth. The oiled sulphide particles float on the surface while the impurities sink to the bottom.

The ore is collected, washed and dried.

- Roasting

The concentrated ore is then heated strongly in air to form zinc oxide.



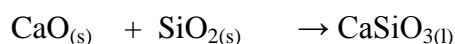
- Reduction

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

Limestone decomposes into calcium oxide and carbondioxide.

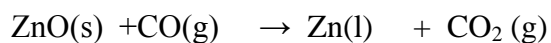
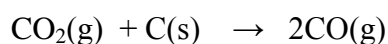
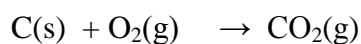


The calcium oxide reacts with silica, one of the impurities to form calcium silicate (slag).



Coke burns to carbon dioxide, which is reduced by unburnt coke to carbon monoxide.

The carbonmonoxide reduces zinc oxide to zinc.



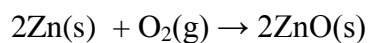
The slag sinks to the bottom and can be removed where as the zinc produced leaves as vapor at the top of the blast furnace where its cooled and allowed to solidify.

## REACTIONS OF ZINC

a) With air

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

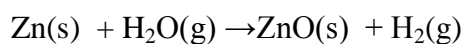
Zinc burns in air (oxygen) to form zinc oxide.



( yellow when hot and white on cooling.)

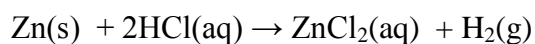
b) With water

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

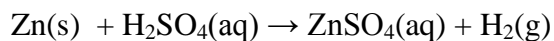


c) With acid

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



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



Reaction of zinc with conc.  $\text{H}_2\text{SO}_4$

produces Zinc sulphate, sulphurdioxide and water as the products.

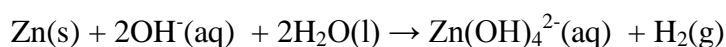


NB:

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

d) With alkalis

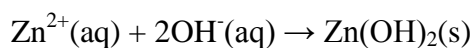
Zinc react with aqueous alkalis to form zincates' complex and hydrogen gas.



## COMPOUNDS OF ZINC

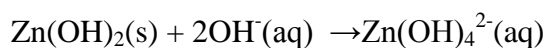
### ZINC HYDROXIDE

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

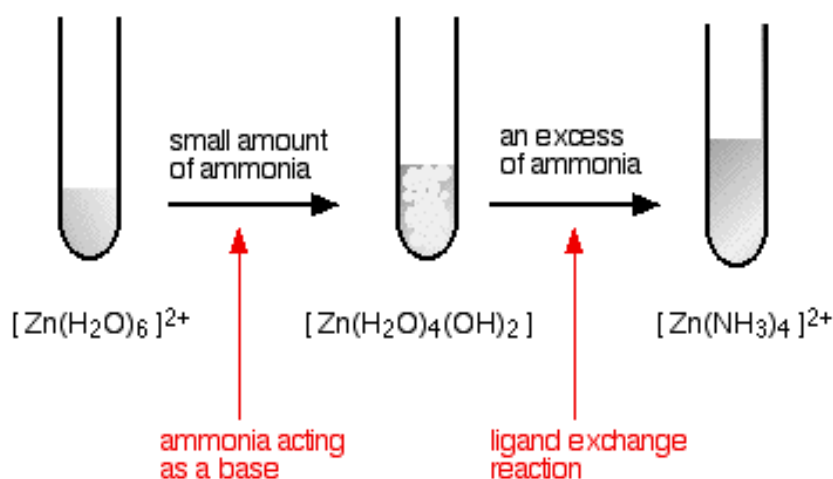
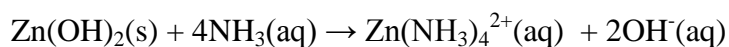


White ppt

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



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

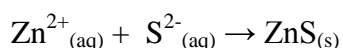
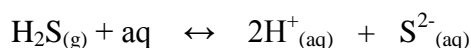


## ZINC SULPHIDE

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

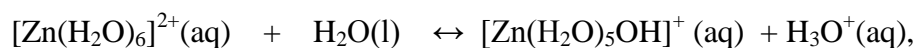
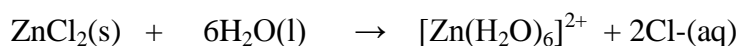
When  $\text{H}_2\text{S}$  gas is passed through a solution of a metallic salt, a metallic sulphide is formed but if the  $\text{H}_2\text{S}$  is passed through an acidic solution of a metallic salt, the sulphide may not be formed.

Explanation:



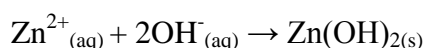
If before bubbling hydrogen sulphide the solution is acidified, the excess  $\text{H}^+$  ions present suppresses the formation of sulphide ions in 1<sup>st</sup> equation above and therefore the concentration of sulphide ions will be too low to precipitate zinc sulphide.

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

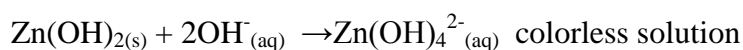


### TEST FOR ZINC IONS

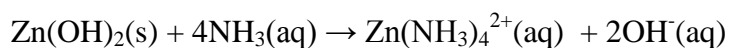
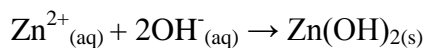
1) Addition of aqueous sodium hydroxide drop wise to a solution of  $\text{Zn}^{2+}$  ions produces a white ppt which dissolves in excess to form a colorless solution.



White ppt



2) Addition of ammonia solution drop wise to a solution of zinc ions, produces a white ppt soluble in excess to form a colorless solution.



3) Addition of potassium ferrocyanide solution to a solution of  $\text{Zn}^{2+}$  ions produces a white ppt. soluble in sodium hydroxide.

4) Addition of ammonium sulphide solution produces a white ppt soluble in dilute HCl acid.

5) Using disodium hydrogen phosphate, white ppt is formed with zinc ions.

### USES OF ZINC

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

Zinc is higher than iron in electrochemical(reactivity) series .

If a galvanized piece of iron developed a small scratch and the iron is exposed, iron does not rust.

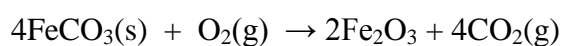
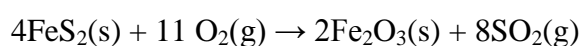
This is because the zinc in the neighborhood of the exposed iron undergoes oxidation in preference to iron forming a thin layer of ZnO which prevents further attack.

## IRON

### Ores of iron:

- Haematite ,  $\text{Fe}_2\text{O}_3$
- Magnetite ,  $\text{Fe}_3\text{O}_4$
- Iron Pyrite ,  $\text{FeS}_2$
- Siderite ,  $\text{FeCO}_3$

The 1<sup>st</sup> two ores are used directly but the last two must be 1<sup>st</sup> roasted in air to convert them to stable iron(iii) oxide. e.g



## EXTRACTION OF IRON

Iron is extracted from its ore called haematite ( $\text{Fe}_2\text{O}_3$ ) in a blast furnace

### The raw materials used in the extraction are:

- ✓ The ore, Haematite
- ✓ Coke

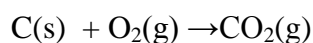
✓ Limestone( calcium carbonate)

✓ Hot air

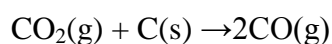
The hot blast of air enters the blast furnace through narrow pipes called Tuyeres located at the lower part of the furnace. The other materials are fed into the furnace from the top.

#### REACTIONS TAKING PLACE IN THE BLAST FURNACE

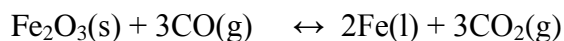
In the presence of hot air coke burns to produce carbondioxide gas



As the carbondioxide ascends, it reacts with unburnt coke to form carbonmonoxide



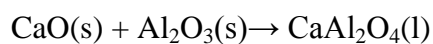
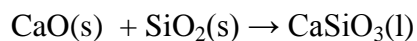
The carbonmonoxide produced reduces the ore to iron.



The role of the limestone is to remove impurities like silica( SiO<sub>2</sub>)



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



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

The molten iron solidifies on cooling to form PIG iron.

Properties of pig iron:



- Low melting point.
- Impure e.g. carbon, silicon, sulphur, etc.

Pig iron can be used in making gas stove, drainage pipes, Bunsen burner bases, boiler plates etc

### **Purification of pig iron.**

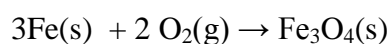
The Bessemer process:

This involves pouring the molten iron into a large tank called the converter and air is blown into it to oxidize the impurities such as carbon, sulphur and phosphorus to their gaseous oxides.

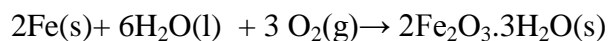
### **REACTIONS OF IRON**

a) With air

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



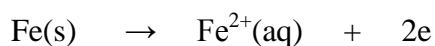
Iron reacts with moist cold air to form brown hydrated iron(iii) oxide or rust.



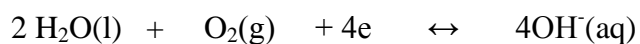
### **How rusting occurs:**

Rusting is an electrochemical process which takes place when different parts of iron act as anode and cathode.

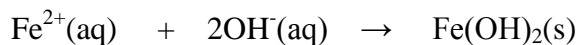
At the cathodic region:



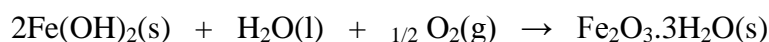
At the anodic region:



If the cathodic and anodic areas are close enough, iron(ii) hydroxide is formed.



Moist air then oxidizes the iron(ii) hydroxide to rust.

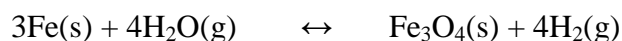


### Prevention of rusting

- Painting
- Greasing
- Galvanizing (coating with zinc)

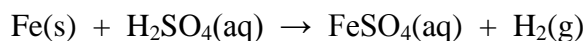
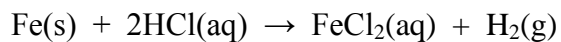
b) With water

Heated iron reacts with steam to form black tri-iron tetra oxide.



c) With acid.

Iron reacts with dilute acids(HCl & H<sub>2</sub>SO<sub>4</sub>) to form hydrogen gas and iron(ii) salts.

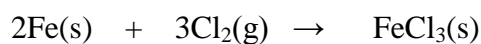


Hot conc. sulphuric acid oxidizes iron to iron(iii) sulphate, sulphur dioxide and water.



d) With halogens.

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



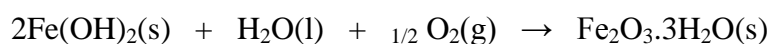
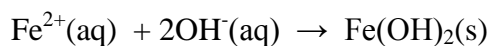
Compounds of iron

### +2 oxidation state

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

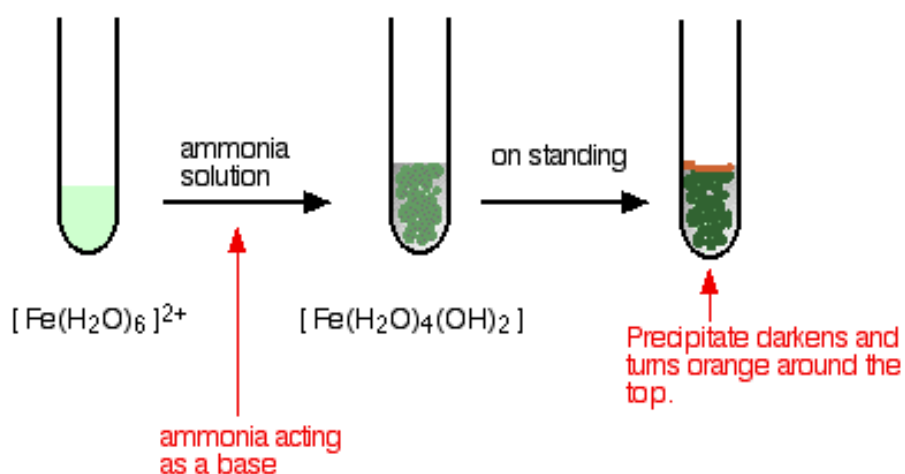
#### a) Iron(ii) hydroxide

It's a green ppt formed when sodium hydroxide solution is added drop wise to a solution of  $\text{Fe}^{2+}$  solution. The ppt is insoluble in excess and turns brown due to aerial oxidation on exposure to air .



NB:

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

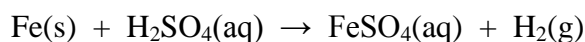


#### b) Hydrated iron(ii) sulphate. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

Its prepared by heating iron fillings with dilute sulphuric acid and crystallizing the salt

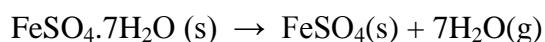
from solution.

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

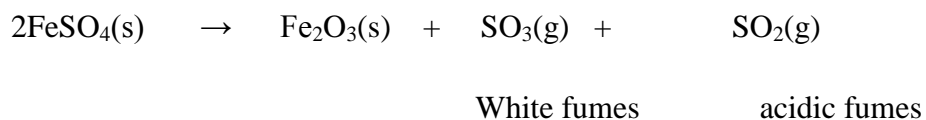


### **Action of heat on hydrated iron(ii) sulphate**

On gentle heating



On further heating.



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

### **+3 oxidation state**

This is the most stable oxidation state of iron.

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

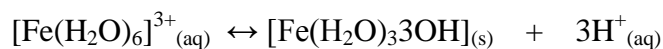
e.g. a solution of iron (iii) chloride turns blue litmus red.

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

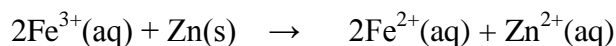


Brown ppt

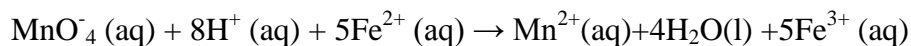
or



On addition of zinc powder to a brown/ yellow solution of iron(iii), the color of the solution changes to green.



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

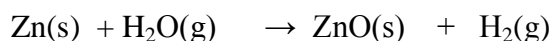


On bubbling hydrogen sulphide gas to a solution containing  $\text{Fe}^{3+}$  ion, the color of the solution changes from yellow to green with formation of a yellow solid.

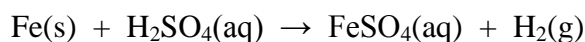


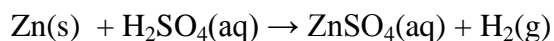
### Similarities in the chemistry of Zn and Fe

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

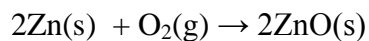
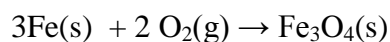


2) Both react with dilute acid ( $\text{HCl}$  &  $\text{H}_2\text{SO}_4$ ) to liberate hydrogen gas.

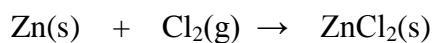
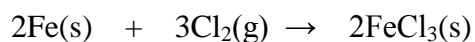




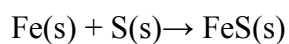
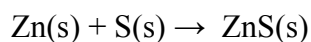
3) Both metal when heated react with oxygen to form oxide.



4) Both metals when heated react with chlorine to form chloride.

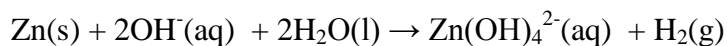


5) Both elements react with sulphur to form sulphide.



### **Differences in the chemistry of Zn & Fe**

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



2) Zn shows a single valency of +2 while iron exhibits variable valencies of +2 & +3.

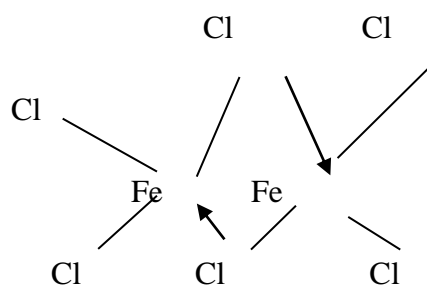
3) Zn forms compounds that are white in color where as Fe forms compounds which are colored.

$\text{Fe}^{2+}$  -green

$\text{Fe}^{3+}$  -brown

4) Iron is paramagnetic(due to unpaired electrons in the 3d-subshell) while Zn is diamagnetic( due to paired electrons in its 3d-subshell)

5) Fe forms dimeric chloride,  $\text{Fe}_2\text{Cl}_6$ .



6) Zinc does not react with cold moist air. Iron reacts with moist air to form hydrated iron(III) oxide (rust).

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

## **COPPER**

Atomic number is 29

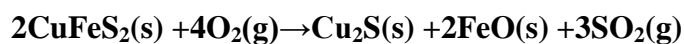
Electronic configuration:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

### ORES OF COPPER

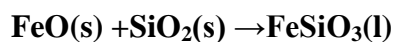
1. copper pyrite  $\text{CuFeS}_2$
2. malachite  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$

Extraction of copper(pyrite ore)

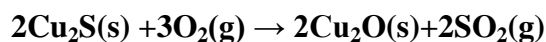
- The ore is 1<sup>st</sup> ground to powder. The finely divided ore is then mixed with water and oil(frothing agent). The earthy materials sink at the bottom because of their high density whereas the ore particles float on top, where they are removed, washed and dried.
- The ore is roasted to convert the copper pyrite to copper(I) sulphide, iron(II) oxide and sulphur dioxide.



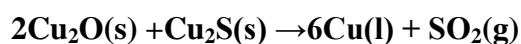
- The solid product is transferred into a blast furnace and silica added. On strong heating, the iron(ii)oxide reacts with silica to form slag.



- The copper(i) sulphide reacts with air forming copper(i)oxide.



- The copper(i)oxide produced and the unroasted copper(i)sulphide react in the heat of the blast furnace with limited air supply to form copper.



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

### **Extraction from malachite**

- Concentration process.

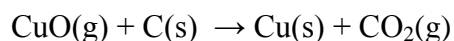
The ore is ground to powder. The finely divided ore particles is mixed with water and oil and shaken for a while.

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

- The ore is roasted to form copper(ii) oxide.



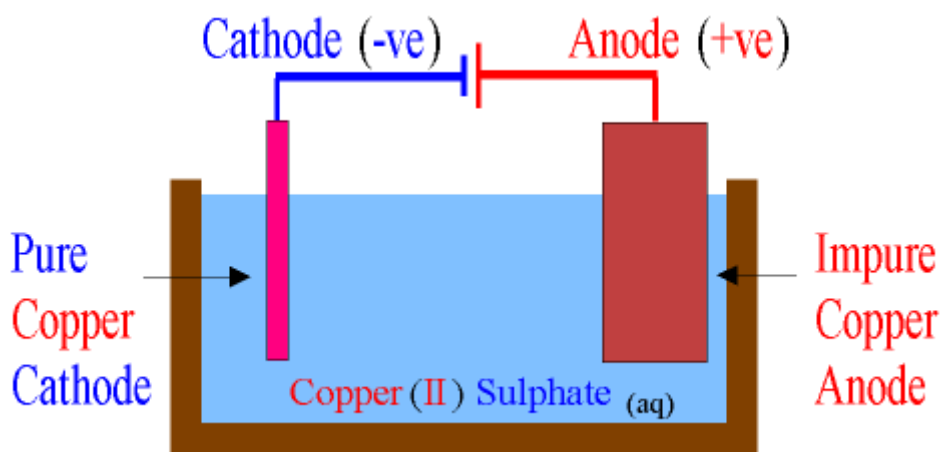
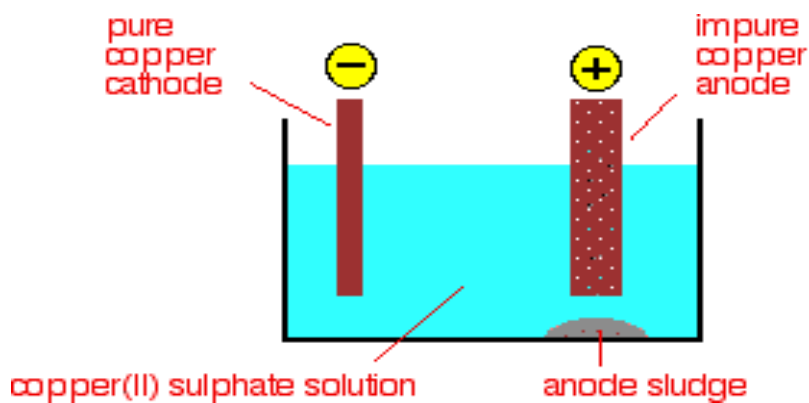
- The copper(ii) oxide is reduced with carbon on heating to copper.



The copper formed is then purified by method of electrolysis.

Purification of Copper –Electrolysis





or

- The anode is a block of impure copper.
- The cathode is a thin piece of pure copper
- The electrolyte is copper(ii) sulphate solution.
- When electricity is passed through the cell,  
At the anode,  
copper is dissolved by oxidation,  $\text{Cu}^{2+}$  ions go into solution.
- $\text{Cu}_{(s)} - 2e^- \rightarrow \text{Cu}^{2+}_{(aq)}$
- At the cathode,
- copper is deposited by reduction.
- $\text{Cu}^{2+}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)}$
- As copper ions move from the anode to the cathode

the anode gets smaller as the cathode gets bigger

## Uses of copper

Amongst other things copper is used for:

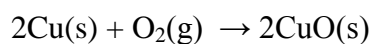
- electrical wiring. It is a very good conductor of electricity and is easily drawn out into wires.
- domestic plumbing. It doesn't react with water, and is easily bent into shape.
- boilers and heat exchangers. It is a good conductor of heat and doesn't react with water.
- making brass. Brass is a copper-zinc alloy. Alloying produces a metal harder than either copper or zinc individually. Bronze is another copper alloy - this time with tin.
- coinage. copper-colored coins, "silver" coins are also copper alloys - this time with nickel. These are known as cupronickel alloys. UK pound coins and the gold-colored bits of euro coins are copper-zinc-nickel alloys.

## REACTIONS OF COPPER

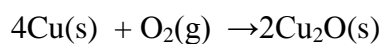
a) With air

Copper reacts with moist air to form a green outer layer of copper(ii)carbonate(protective layer).

Heated copper reacts with oxygen enriched air(below 800 °C) to form black copper(ii) oxide.

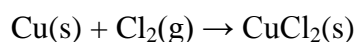


At very high temperature  $> 800\text{ }^{\circ}\text{C}$ , copper reacts with oxygen to form copper(i)oxide.



b) With halogens.

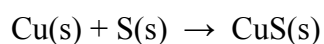
Heated copper reacts with halogen to form copper(ii)halide.



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

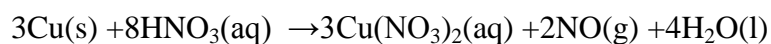
c) With sulphur.

When heated, copper forms a sulphide .

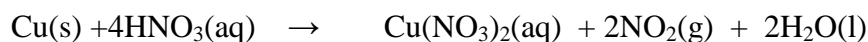


d) With acids.

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



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



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



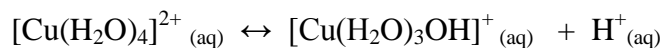
## COMPOUNDS OF COPPER

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

Compounds in +2 oxidation states

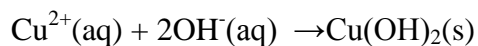
This is the most stable oxidation state of copper and in aqueous solution exists as  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  which is a blue solution.

It slowly undergoes hydrolysis forming acidic solution.

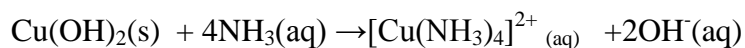


### (i) Copper(ii) hydroxide

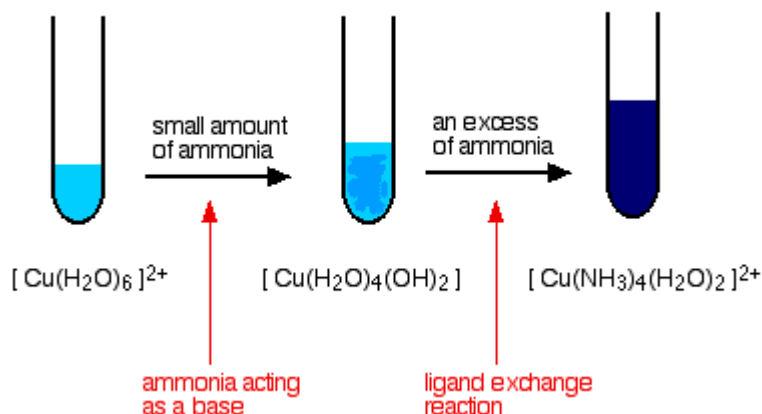
It's a blue ppt formed when aqueous sodium hydroxide is added to copper(ii) ions.



Copper(ii) hydroxide does not dissolve in excess sodium hydroxide. However dissolves in excess ammonia solution to form a deep blue solution.

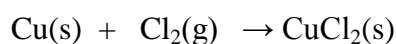


Tetra- ammine copper(ii) ions



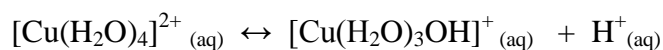
ii) Copper (ii)chloride.

Its prepared by adding a stream of dry chlorine gas over heated copper metal.



In aqueous solution, it exists as  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ .

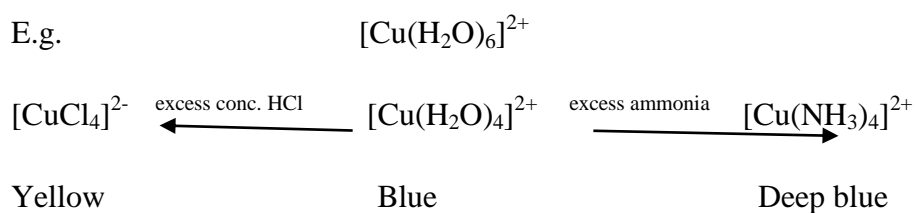
It slowly undergoes hydrolysis forming acidic solution.



Copper(ii) chloride dissolves in conc. hydrochloride acid to form a yellow solution of tetra-chlorocuprate(ii) ions  $[\text{CuCl}_4]^{2-}$

NB:

A complex ion may undergo ligand exchange whereby all its ligands are replaced by a different ligand which is more willing to donate the pair of electrons more readily. Altering a ligand around a central metal ion brings about a marked color change.



## DETERMINATION OF COPPER(II) IONS IN COPPER(II) SALTS

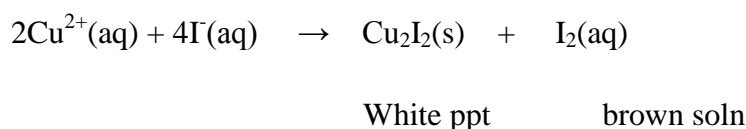
### Method 1

Applicable to any soluble salt of copper.

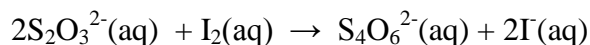
(starting from copper ore, dissolve the ore in dilute sulphuric acid)

Procedure:

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



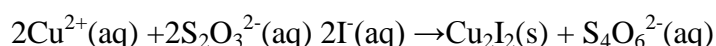
The amount of iodine liberated is then determined by titrating the resultant solution with a standard solution of sodium thiosulphate using starch indicator.



The volume of thiosulphate solution used is noted.

### Treatment of results

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

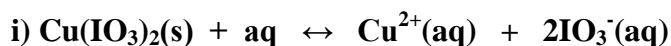


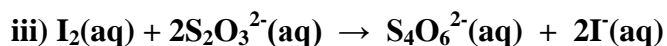
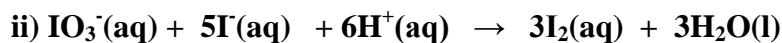
2 moles of thiosulphate ions react with 2 moles of  $\text{Cu}^{2+}$  ions .

Thus knowing the moles of thiosulphate ions that reacted , that of copper ions present in the solution can be determined.

### Method 2

This method applies to copper(ii) iodate only  $\text{Cu}(\text{IO}_3)_2$





To a solution containing copper(ii) iodate is added excess potassium iodide solution followed by dilute sulphuric acid .

Iodine is liberated according to the equations above. The liberated iodine is then titrated with a standard solution of sodium thiosulphate using starch as indicator.

The volume of thiosulphate used is noted.

## MANGANESE

a) Write the electronic configuration of the following species (atomic number= 25):

i) Mn

ii)  $\text{Mn}^{2+}$

iii)  $\text{Mn}^{3+}$

iv)  $\text{Mn}^{7+}$

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

ii) State the possible oxidation states of manganese.

iii) Explain why manganese show variable oxidation states.

c) Aqueous sodium hydroxide was added drop wise to a solution containing  $\text{Mn}^{2+}$ , state what was observed and write equation for the reaction that took place.

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

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

e) Write equation to show the reduction of  $\text{MnO}_4^-$  in :

i) alkaline medium.

ii) acidic medium.

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

**Answer**

i)  $1\text{S}^22\text{S}^22\text{P}^63\text{S}^23\text{P}^64\text{S}^23\text{d}^5$

ii)  $1\text{S}^22\text{S}^22\text{P}^63\text{S}^23\text{P}^63\text{d}^5$

iii)  $1\text{S}^22\text{S}^22\text{P}^63\text{S}^23\text{P}^63\text{d}^4$

iv)  $1\text{S}^22\text{S}^22\text{P}^63\text{S}^23\text{P}^6$

i) The most stable oxidation state is +2. This is because after using the 4s-electrons, a half filled 3d-orbital that is stable is left.

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

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

iii) The variable oxidation state of manganese is due to the fact that both the 4s and the 3d- electrons take part in bond formation.

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

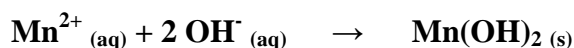
For +2 oxidation state, only the 4s-electrons are utilized for bond formation, forming stable  $\text{Mn}^{2+}$ . For higher oxidation states, both the 4s and 3d- electrons are utilized.

**Observation:**

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

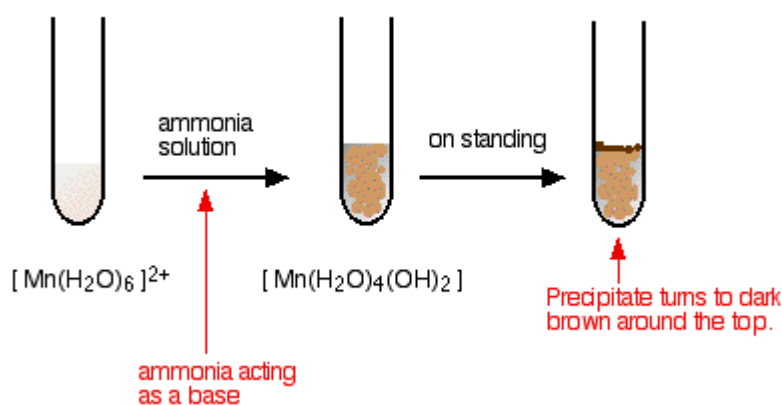
**Equation:**





NB:

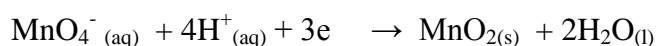
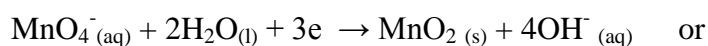
Similar observation & reaction occurs with aqueous ammonia solution.



d) i)  $\text{MnO}_4^-$

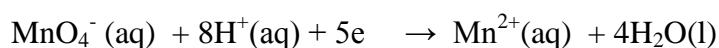
ii) Manganese  $1\text{S}^2 2\text{S}^2 2\text{P}^6 3\text{S}^2 3\text{P}^6 4\text{S}^2 3\text{d}^5$ , shows an oxidation state of +7 by using both the 4s and 3d- electrons in the bond formation because they are energetically similar.

e) i)



In alkaline condition, the change in oxidation state is from  $+7$  to  $+4$  since potassium manganate (vii) is a mild oxidizing agent in alkaline medium

ii)



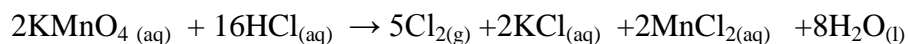
NB:  $\text{KMnO}_4$  has a wide applications in the laboratory as an oxidizing agent which include the following:

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

- To test for reducing agents e.g. sulphur dioxide.
- Estimating iron (ii) salts and oxalates.
- Preparation of gases e.g. chlorine gas is liberated when conc hydrochloric acid is reacted with it.

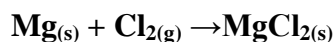
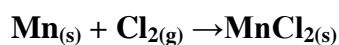
NB:

Hydrochloric acid is not used to acidify  $\text{KMnO}_4$  during titration because  $\text{KMnO}_4$  is a very strong oxidizing agent, oxidizes  $\text{Cl}^-$  ions from hydrochloric acid to chlorine which colors the whole solution pale green and difficult to estimate end point.

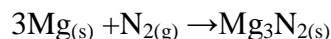
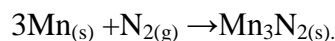


f)

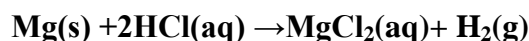
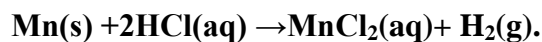
- They both react with chlorine to form chloride when heated.



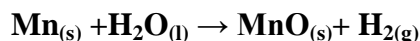
- They both react directly with nitrogen to form similar nitrides

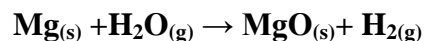


- They both react with dilute hydrochloric acid to liberate hydrogen gas.



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



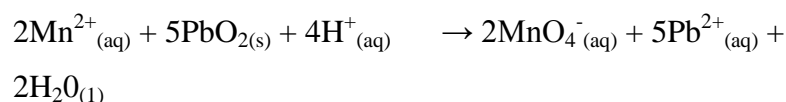
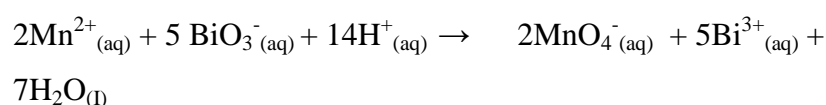


NB:

Confirmatory test of Manganese,  $\text{Mn}^{2+}$  ions in solution.

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

A purple solution forms

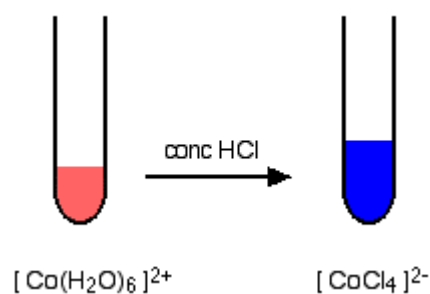


### Reaction of Cobalt (II) ion, $\text{Co}^{2+}$

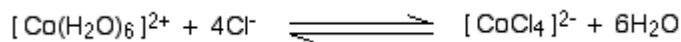
The (+2) oxidation state is the most stable for simple cobalt salts; they are colored pink. The simplest ion that cobalt forms in solution is the pink hexaaquacobalt(II) ion -  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ .

A ligand exchange reaction involving chloride ions

If you add concentrated hydrochloric acid to a solution containing hexaaquacobalt(II) ions, the solution turns from its original pink colour to a rich blue. The six water molecules are replaced by four chloride ions.



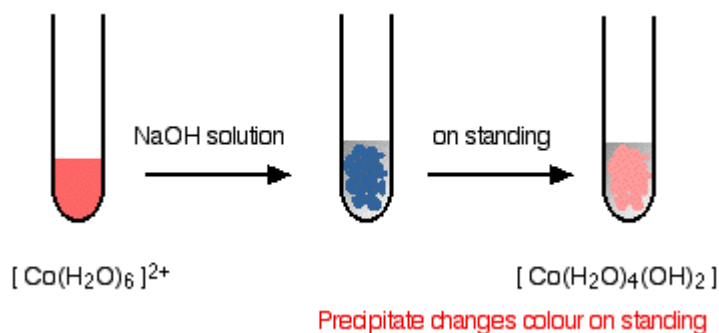
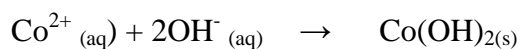
The reaction taking place is reversible.



If you add water to the blue solution, it returns to the pink colour.

a) Sodium hydroxide solution

A blue precipitate formed insoluble in excess and turns pink on standing

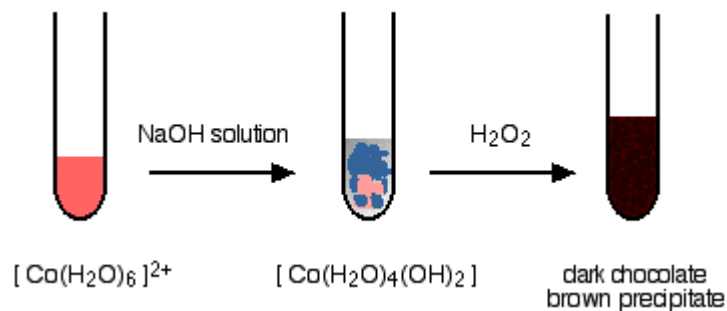


With sodium hydroxide solution and hydrogen peroxide

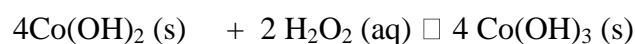
Rather than relying on oxidation by the air, you can add an oxidising agent such as hydrogen peroxide

You get the cobalt(II) hydroxide complex when you add the sodium hydroxide solution.

Addition of hydrogen peroxide produces lots of bubbles of oxygen and a dark chocolate brown precipitate.

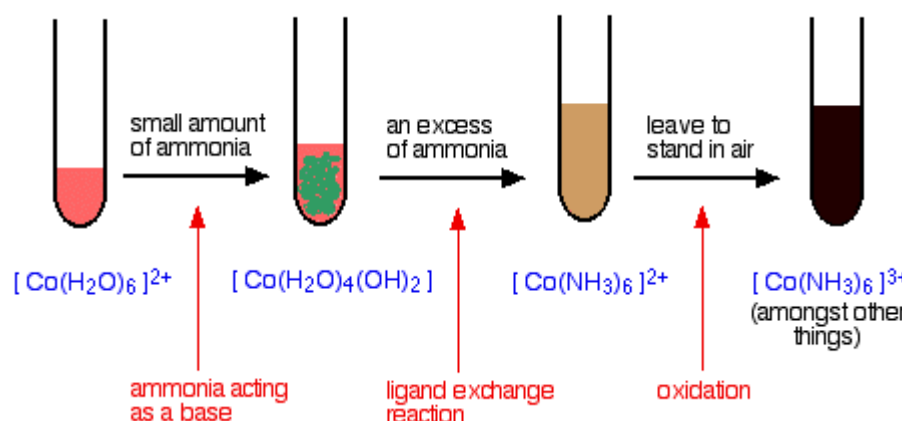
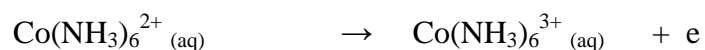
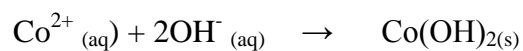


The final precipitate contains cobalt in the +3 oxidation state.



### b) Ammonia Solution

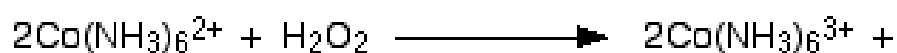
A blue precipitate formed which dissolves in excess to form a brown solution and turns to a deep red-brown solution on standing in air.



With ammonia solution and hydrogen peroxide

Rather than relying on oxidation by the air, you can add an oxidising agent such as hydrogen peroxide

The reaction with ammonia solution followed by hydrogen peroxide produces the same dark reddish-brown solution as before - only faster. The equation for the oxidation of the ammine complex is:



Reactions of Nickel (II) Ion,  $\text{Ni}^{2+}$

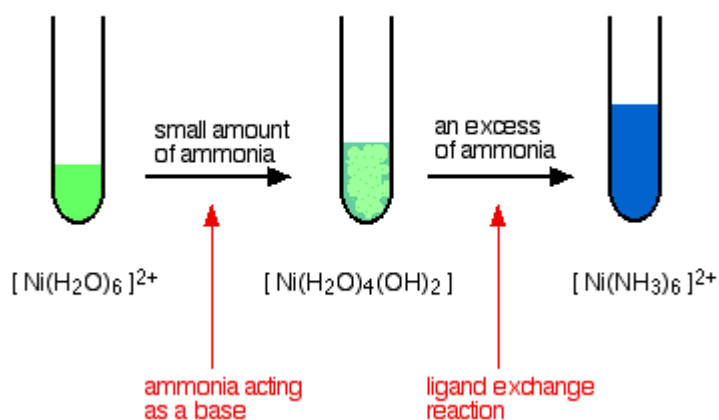
a) Sodium hydroxide solution

A green precipitate insoluble in excess formed.



b) Ammonia Solution

A green precipitate formed which dissolves in excess to form a blue solution



c) Dimethylglyoxime

**Test**

To the solution of  $\text{Ni}^{2+}$  is 1<sup>st</sup> added ammonia solution drop-wise until excess followed by a drop of dimethylglyoxime solution.

**Observation**

A green ppt, soluble to form blue solution and red precipitate is formed .