

## 4. Inorganic Chemistry and the Periodic Table

### 4A: Group 2

#### Atomic radius

Atomic **radius increases** down the Group.  
As one goes down the group, the atoms have **more shells of electrons** making the atom bigger.

#### Melting points

Down the group the melting **points decrease**. The **metallic bonding** weakens as the **atomic size increases**. The distance between the positive ions and delocalized electrons increases. Therefore the electrostatic attractive forces between the **positive ions** and the **delocalized electrons** weaken.

#### 1st ionisation energy

The outermost electrons are held more weakly because they are **successively further from the nucleus** in additional shells.

In addition, the outer shell electrons become **more shielded** from the attraction of the nucleus by the repulsive force of inner shell electrons

#### Group 2 reactions

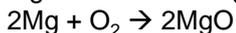
Reactivity of group 2 metals **increases** down the group

The reactivity increases down the group as the atomic radii increase there is more shielding. The nuclear attraction decreases and it is easier to remove (outer) electrons and so cations form more easily

#### Reactions with oxygen.

The group 2 metals will burn in oxygen.

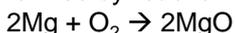
Mg burns with a bright white flame.



MgO is a white solid with a high melting point due to its ionic bonding.

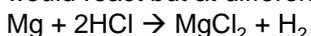
Mg will also react slowly with oxygen without a flame.

Mg ribbon will often have a thin layer of magnesium oxide on it formed by reaction with oxygen.



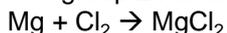
This needs to be cleaned off by emery paper before doing reactions with Mg ribbon.

If testing for reaction rates with Mg and acid, an un-cleaned Mg ribbon would give a false result because both the Mg and MgO would react but at different rates.



#### Reactions with chlorine

The group 2 metals will react with chlorine

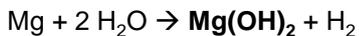


#### Reactions with water.

Magnesium burns **in steam** to produce **magnesium oxide** and hydrogen. The Mg would burn with a bright white flame.

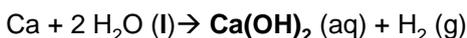


Mg will also react with warm water, giving a different **magnesium hydroxide** product.



This is a much slower reaction than the reaction with steam and there is no flame.

The other group 2 metals will react with **cold water** with increasing vigour down the group to form **hydroxides**.



The hydroxides produced make the water alkaline

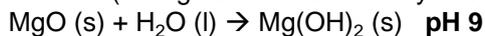
One would observe:

- fizzing, (more vigorous down group)
- the metal dissolving, (faster down group)
- the solution heating up (more down group)
- and with calcium a white precipitate appearing (less precipitate forms down group)

## Reactions of the Oxides of Group 2 elements with water

**Group 2 ionic oxides** react with water to form hydroxides

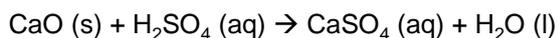
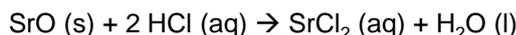
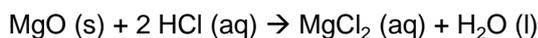
The ionic oxides are basic as the oxide ions accept protons to become hydroxide ions in this reaction (acting as a bronsted lowry base)



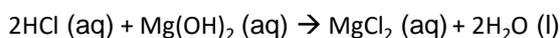
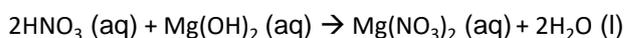
$\text{Mg(OH)}_2$  is only slightly soluble in water so fewer free  $\text{OH}^-$  ions are produced and so lower pH



## Reactions of the Oxides of Group 2 elements with Acids



## Reactions of the hydroxides of Group 2 elements with Acids



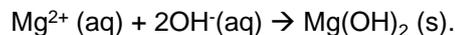
### Solubility of hydroxides

Group II hydroxides become **more soluble** down the group.

All Group II hydroxides when not soluble appear as white precipitates.

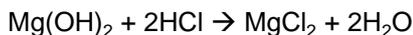
Magnesium hydroxide is classed as insoluble in water.

**Simplest Ionic Equation** for formation of  $\text{Mg(OH)}_2$  (s)



A suspension of magnesium hydroxide in water will appear slightly alkaline (pH 9) so some hydroxide ions must therefore have been produced by a very slight dissolving.

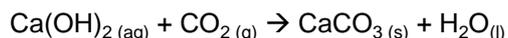
Magnesium hydroxide is used in medicine (in suspension as milk of magnesia) to neutralise excess acid in the stomach and to treat constipation.



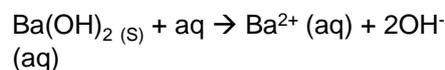
It is safe to use because it so weakly alkaline. It is preferable to using calcium carbonate as it will not produce carbon dioxide gas.

Calcium hydroxide is reasonably soluble in water. It is used in agriculture to neutralise acidic soils.

An aqueous solution of calcium hydroxide is called lime water and can be used a test for carbon dioxide. The limewater turns cloudy as white calcium carbonate is produced.



Barium hydroxide would easily dissolve in water. The hydroxide ions present would make the solution strongly alkaline.

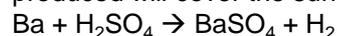


### Solubility of Sulphates

Group II sulphates become **less soluble** down the group.

$\text{BaSO}_4$  is the least soluble.

If Barium metal is reacted with sulphuric acid it will only react slowly as the insoluble Barium sulphate produced will cover the surface of the metal and act as a barrier to further attack.



The same effect will happen to a lesser extent with metals going up the group as the solubility increases. The same effect does not happen with other acids like hydrochloric or nitric as they form soluble group 2 salts.

## Thermal decomposition of Group 2 carbonates

Group 2 carbonates decompose on heating to produce group 2 oxides and carbon dioxide gas.



Group 2 carbonates are more thermally stable as you go down the group. As the cations get bigger they have less of a polarising effect and distort the carbonate ion less. The C-O bond is weakened less so it less easily breaks down

Group 1 carbonates do not decompose with the exception of Lithium. As they only have +1 charges they don't have a big enough charge density to polarise the carbonate ion. Lithium is the exception because its ion is small enough to have a polarising effect

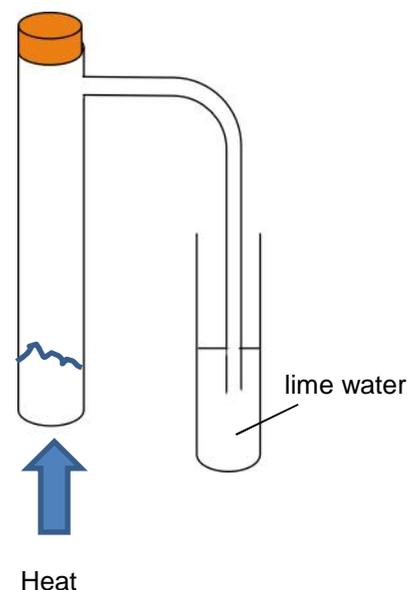


There are a number of experiments that can be done to investigate the ease of decomposition.

One is to heat a known mass of carbonate in a side arm boiling tube and pass the gas produced through lime water. Time for the first permanent cloudiness to appear in the limewater. Repeat for different carbonates using the same moles of carbonate/same volume of limewater/same Bunsen flame and height of tube above flame.

**Thermal decomposition** is defined as the use of heat to break down a reactant into more than one product

The ease of thermal decomposition **decreases** down the group



## Thermal decomposition of Group 2 Nitrates

Group 2 nitrates decompose on heating to produce group 2 oxides, oxygen and nitrogen dioxide gas.

You would observe brown gas evolving ( $\text{NO}_2$ ) and the white nitrate solid is seen to melt to a colourless solution and then resolidify



The ease of thermal decomposition **decreases** down the group

The explanation for change in thermal stability is the same as for carbonates. Magnesium nitrate decomposes the easiest because the  $\text{Mg}^{2+}$  ion is smallest and has the greater charge density. It causes more polarisation of the nitrate anion and weakens the N-O bond

Group 1 nitrate do not decompose in the same way as group 2 with the exception of Lithium nitrate. They decompose to give a Nitrate (III) salt and oxygen.



Sodium Nitrate(V)      Sodium Nitrate(III)

Lithium nitrate decomposes in the same way as group 2 nitrates



## Flame tests

### Method

Use a **nichrome wire** ( nichrome is an unreactive metal and will not give out any flame colour)

Clean the wire by dipping **in concentrated hydrochloric acid** and then heating in Bunsen flame

If the sample is not powdered then grind it up.

Dip wire in solid and put in bunsen flame and observe flame

### Explanation for occurrence of flame

In a flame test the heat causes the electron to move to a higher energy level.

The electron is unstable at the higher energy level and so drops back down. As it drops **back down from the higher to a lower energy level**, energy is emitted in the form of visible light energy with the wavelength of the observed light

Lithium : Scarlet red

Sodium : Yellow

Potassium : lilac

Rubidium : red

Caesium: blue

Magnesium: no flame colour (energy emitted of a wavelength outside visible spectrum)

Calcium: brick red

Strontium: red

Barium: apple green

## 4B Halogens

Fluorine (F<sub>2</sub>): very pale yellow gas. It is highly reactive  
Chlorine : (Cl<sub>2</sub>) greenish, reactive gas, poisonous in high concentrations  
Bromine (Br<sub>2</sub>) : red liquid, that gives off dense brown/orange poisonous fumes  
Iodine (I<sub>2</sub>) : shiny grey solid sublimes to purple gas.

### Trend in melting point and boiling point

Increase down the group

As the molecules become larger they have more electrons and so have larger London forces between the molecules. As the intermolecular forces get larger more energy has to be put into break the forces. This increases the melting and boiling points

### Trend in electronegativity

*Electronegativity is the relative tendency of an atom in a molecule to attract electrons in a covalent bond to itself.*

As one goes down the group the electronegativity of the elements decreases.

As one goes down the group the atomic radii increases due to the increasing number of shells. The nucleus is therefore less able to attract the bonding pair of electrons

The reactivity of the halogens decreases down the group as the atoms get bigger with more shielding so they less easily attract and accept electrons. They therefore form -1 ions less easily down the group

### 1. The oxidation reactions of halide ions by halogens.

A halogen that is a strong oxidising agent will displace a halogen that has a lower oxidising power from one of its compounds

The oxidising strength decreases down the group. Oxidising agents are electron acceptors.

Chlorine will displace both bromide and iodide ions; bromine will displace iodide ions

know these observations !

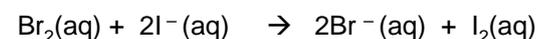
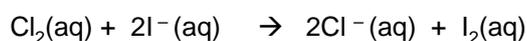
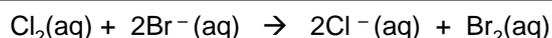
	Chlorine (aq)	Bromine (aq)	Iodine (aq)
potassium chloride (aq)	<i>Very pale green solution, no reaction</i>	<i>Yellow solution, no reaction</i>	<i>Brown solution, no reaction</i>
potassium bromide (aq)	Yellow solution, Cl has displaced Br	<i>Yellow solution, no reaction</i>	<i>Brown solution, no reaction</i>
potassium iodide (aq)	Brown solution, Cl has displaced I	Brown Solution, Br has displaced I	Brown Solution, no reaction

The colour of the solution in the test tube shows which free halogen is present in solution. Chlorine = very pale green solution (often colourless), Bromine = **yellow solution** Iodine = **brown solution** (sometimes black solid present)

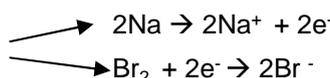
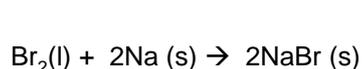
### Observations if an organic solvent is added

	Chlorine (aq)	Bromine (aq)	Iodine (aq)
potassium chloride (aq)	colourless, no reaction	yellow, no reaction	purple, no reaction
potassium bromide (aq)	yellow, Cl has displaced Br	yellow, no reaction	purple, no reaction
potassium iodide (aq)	purple, Cl has displaced I	purple, Br has displaced I	purple, no reaction

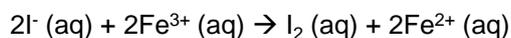
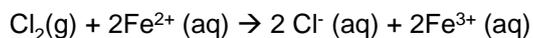
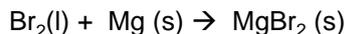
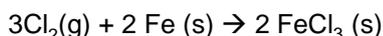
The colour of the organic solvent layer in the test tube shows which free halogen is present in solution. Chlorine = colourless Bromine = **yellow** Iodine = **purple**



## The oxidation reactions of metals and metal ion by halogens.



In all reactions where halogens are reacting with metals, the metals are being oxidised



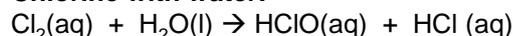
Chlorine and Bromine can oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Iodine is not strong enough oxidising agent to do this reaction. The reaction is reversed for Iodine

## The disproportionation reactions of chlorine and chlorate(I).

Disproportionation is the name for a reaction where an element simultaneously oxidises and reduces.

Chlorine is both simultaneously reducing and oxidising changing its oxidation number from 0 to -1 and 0 to +1

### Chlorine with water:



If some universal indicator is added to the solution it will first turn red due to the acidity of both reaction products. It will then turn colourless as the HClO bleaches the colour.

The pale greenish colour of these solutions is due to the  $\text{Cl}_2$

Chlorine is used in water treatment to kill bacteria. It has been used to treat drinking water and the water in swimming pools. The benefits to health of water treatment by chlorine outweigh its toxic effects.

### Reaction of halogens with cold dilute NaOH solution:

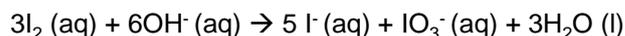
$\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  in aqueous solutions will react with cold sodium hydroxide. The colour of the halogen solution will fade to colourless



The mixture of NaCl and NaClO is used as Bleach and to disinfect/ kill bacteria

### Reaction of halogens with hot dilute NaOH solution:

With hot alkali disproportionation also occurs but the halogen that is oxidised goes to a higher oxidation state.



In IUPAC convention the various forms of sulfur and chlorine compounds where oxygen is combined are all called sulfates and chlorates with relevant oxidation number given in roman numerals. If asked to name these compounds remember to add the oxidation number.

NaClO: sodium chlorate(I)

NaClO<sub>3</sub>: sodium chlorate(V)

K<sub>2</sub>SO<sub>4</sub> potassium sulfate(VI)

K<sub>2</sub>SO<sub>3</sub> potassium sulfate(IV)

## The reaction of halide salts with concentrated sulphuric acid.

The Halides show increasing power as reducing agents as one goes down the group. This can be clearly demonstrated in the various reactions of the solid halides with concentrated sulphuric acid.

**Know the equations and observations of these reactions very well.**

### Explanation of differing reducing power of halides

A reducing agent donates electrons.

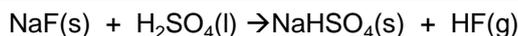
The reducing power of the halides increases down group 7

They have a greater tendency to donate electrons.

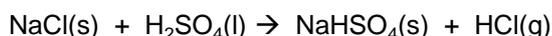
This is because as the ions get bigger it is easier for the outer electrons to be given away as the pull from the nucleus on them becomes smaller.

### Fluoride and Chloride

The  $\text{H}_2\text{SO}_4$  is not strong enough an oxidising reagent to oxidise the chloride and fluoride ions. No redox reactions occur. Only acid-base reactions occur.



Observations: White steamy fumes of HF are evolved.

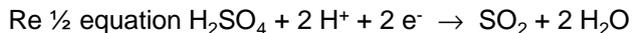
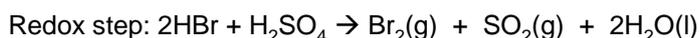


Observations: White steamy fumes of HCl are evolved.

These are acid-base reactions and not redox reactions.  $\text{H}_2\text{SO}_4$  plays the role of an acid (proton donor).

### Bromide

**Br-** ions are stronger reducing agents than **Cl-** and **F-** and after the initial acid-base reaction reduce the Sulphur in  $\text{H}_2\text{SO}_4$  from +6 to +4 in  $\text{SO}_2$



**Observations:** White steamy fumes of HBr are evolved.

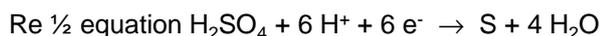
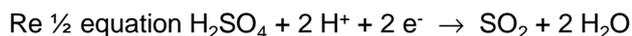
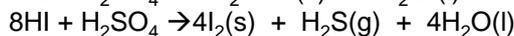
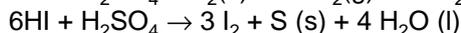
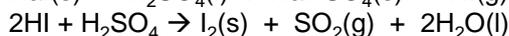
Red fumes of Bromine are also evolved and a colourless, acidic gas  **$\text{SO}_2$**

Reduction product = sulphur dioxide

Note the  $\text{H}_2\text{SO}_4$  plays the role of acid in the first step producing HBr and then acts as an oxidising agent in the second redox step.

### Iodide

**I-** ions are the strongest halide reducing agents. They can reduce the Sulphur from +6 in  $\text{H}_2\text{SO}_4$  to +4 in  $\text{SO}_2$ , to 0 in S and -2 in  $\text{H}_2\text{S}$ .



### Observations:

White **steamy fumes** of HI are evolved.

**Black solid** and **purple fumes** of Iodine are also evolved

A **colourless**, acidic **gas**  $\text{SO}_2$

A **yellow solid** of Sulphur

**$\text{H}_2\text{S}$**  (Hydrogen Sulphide), a **gas** with a **bad egg smell**,

Reduction products = sulphur dioxide, sulphur and hydrogen sulphide

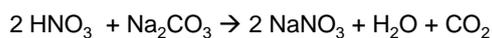
Note the  $\text{H}_2\text{SO}_4$  plays the role of acid in the first step producing HI and then acts as an oxidising agent in the three redox steps

*Often in exam questions these redox reactions are worked out after first making the half-equations*

## The reactions of halide ions with silver nitrate.

This reaction is used as a test to identify which halide ion is present. The test solution is made acidic with **nitric acid**, and then **Silver nitrate solution** is added dropwise.

The role of nitric acid is to react with any carbonates present to prevent formation of the precipitate  $\text{Ag}_2\text{CO}_3$ . This would mask the desired observations



Fluorides produce no precipitate  
Chlorides produce a **white precipitate**  
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$   
Bromides produce a **cream precipitate**  
 $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$   
Iodides produce a **pale yellow precipitate**  
 $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

### Effect Of ammonia on Silver Halides

The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:

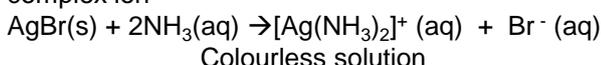
### Effect Of Light on Silver Halides

The precipitates ( except AgI) darken in sunlight forming silver. This reaction is used in photography to form the dark bits on photographic film

**Silver chloride** dissolves in **dilute ammonia** to form a complex ion



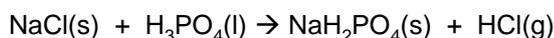
**Silver bromide** dissolves in **concentrated ammonia** to form a complex ion



**Silver iodide** does not react with ammonia – it is too insoluble.

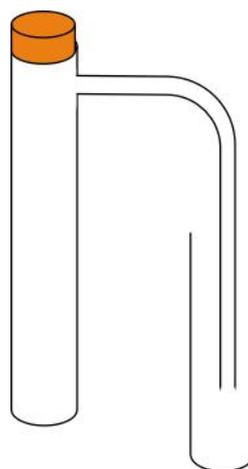
## Producing hydrogen halides

Hydrogen halides are made by the reaction of solid sodium halide salts with phosphoric acid



**Observations:** White steamy fumes of the Hydrogen Halides are evolved.

The Steamy fumes of HCl are produced when the HCl meets the air because it dissolves in the moisture in the air



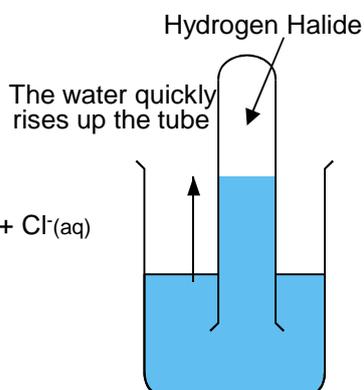
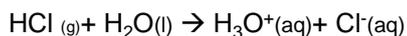
This is the apparatus used to make the hydrogen halide using phosphoric acid.

Notice the downward delivery which is used because the hydrogen halides are more dense than air

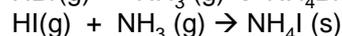
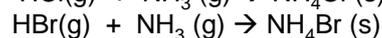
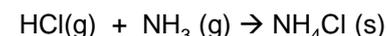
Phosphoric acid is not an oxidising agent and so does not oxidise HBr and HI. Phosphoric acid is more suitable for producing hydrogen halides than the ones with concentrated sulphuric acid to make HCl, HBr, and HI because there are no extra redox reactions taking place and no other products

### Solubility in water :

The hydrogen halides are all soluble in water. They dissolve to form acidic solutions.



All the hydrogen halides react readily with ammonia to give the **white smoke** of the ammonium halide



This can be used as a test for the presence of hydrogen halides

## 4C Analysis of Inorganic Compounds

### Testing for Negative ions (anions)

#### Testing for Presence of a carbonate $\text{CO}_3^{2-}$ and hydrogencarbonates $\text{HCO}_3^-$

Add any dilute acid and observe effervescence.

Bubble gas through limewater to test for  $\text{CO}_2$  – will turn limewater cloudy

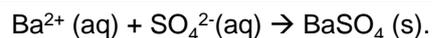
Fizzing due to  $\text{CO}_2$  would be observed if a carbonate or a hydrogencarbonate was present



#### Testing for Presence of a sulfate

**Acidified**  $\text{BaCl}_2$  solution is used as a reagent to test for sulfate ions

If **Barium Chloride** is added to a solution that contains sulfate ions a **white precipitate** forms



Other anions should give a negative result which is no precipitate forming

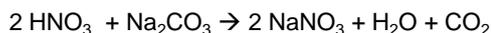
The acid is needed to react with carbonate impurities that are often found in salts which would form a white Barium carbonate precipitate and so give a false result

Sulfuric acid cannot be used to acidify the mixture because it contains sulfate ions which would form a precipitate

#### Testing for halide ions with silver nitrate.

This reaction is used as a test to identify which halide ion is present. The test solution is made acidic with **nitric acid**, and then **Silver nitrate solution** is added dropwise.

The role of nitric acid is to react with any carbonates present to prevent formation of the precipitate  $\text{Ag}_2\text{CO}_3$ . This would mask the desired observations

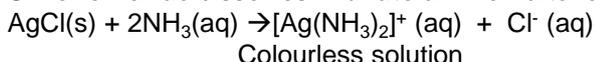


Fluorides produce no precipitate  
Chlorides produce a **white** precipitate  
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$   
Bromides produce a **cream** precipitate  
 $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$   
Iodides produce a **pale yellow** precipitate  
 $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

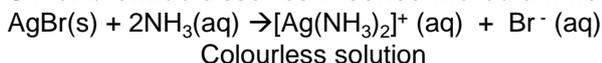
Hydrochloric acid cannot be used to acidify the mixture because it contains chloride ions which would form a precipitate

The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:

**Silver chloride** dissolves in **dilute ammonia** to form a complex ion



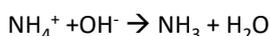
**Silver bromide** dissolves in **concentrated ammonia** to form a complex ion



**Silver iodide** does not react with ammonia – it is too insoluble.

#### Testing for positive ions (cations)

Test for ammonium ion  $\text{NH}_4^+$ , by reaction with warm  $\text{NaOH}(\text{aq})$  forming  $\text{NH}_3$



Ammonia gas can be identified by its pungent smell or by turning red litmus paper blue

See flame tests on page 4 for more cation tests