3. Group 2 and Group 7
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
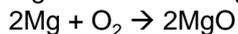
Group 2 reactions

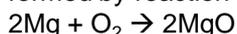Reactivity of group 2 metals **increases** down the group

Reactions with oxygen.

The group 2 metals will burn in oxygen.
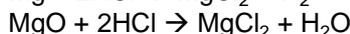Mg burns with a bright white flame.
$2Mg + O_2 \rightarrow 2MgO$

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.
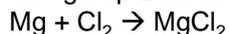$2Mg + O_2 \rightarrow 2MgO$
This needs to be cleaned off by emery paper before doing reactions with Mg ribbon.
If testing for reaction rates with Mg and acid, an un-cleaned Mg ribbon would give a false result because both the Mg and MgO would react but at different rates.
$Mg + 2HCl \rightarrow MgCl_2 + H_2$
$MgO + 2HCl \rightarrow MgCl_2 + H_2O$

Reactions with chlorine

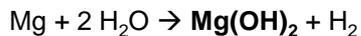The group 2 metals will react with chlorine
$Mg + Cl_2 \rightarrow MgCl_2$

Reactions with water.

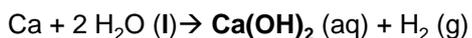Magnesium burns **in steam** to produce **magnesium oxide** and hydrogen. The Mg would burn with a bright white flame.

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

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

$Mg + 2 H_2O \rightarrow Mg(OH)_2 + H_2$

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.**

$Ca + 2 H_2O (l) \rightarrow Ca(OH)_2 (aq) + H_2 (g)$

$Sr + 2 H_2O (l) \rightarrow Sr(OH)_2 (aq) + H_2 (g)$

$Ba + 2 H_2O (l) \rightarrow Ba(OH)_2 (aq) + H_2 (g)$

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

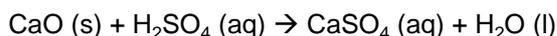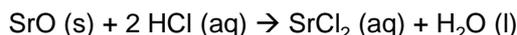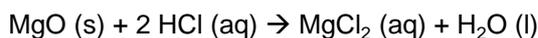**Group 2 ionic oxides** react with water to form hydroxides

The ionic oxides are basic as the oxide ions accept protons to become hydroxide ions in this reaction (acting as a bronsted lowry base)
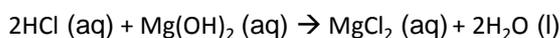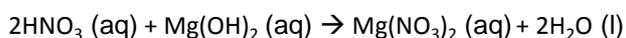
MgO (s) + H_2O (l) → $Mg(OH)_2$ (s)   **pH 9**
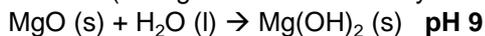
$Mg(OH)_2$ is only slightly soluble in water so fewer free OH^- ions are produced and so lower pH

CaO (s) + H_2O (l) → $Ca(OH)_2$ (aq)   **pH 12**

Reactions of the Oxides of Group 2 elements with Acids

MgO (s) + 2 HCl (aq) → $MgCl_2$ (aq) + H_2O (l)

SrO (s) + 2 HCl (aq) → $SrCl_2$ (aq) + H_2O (l)

CaO (s) + H_2SO_4 (aq) → $CaSO_4$ (aq) + H_2O (l)

Reactions of the hydroxides of Group 2 elements with Acids

$2HNO_3$ (aq) + $Mg(OH)_2$ (aq) → $Mg(NO_3)_2$ (aq) + $2H_2O$ (l)

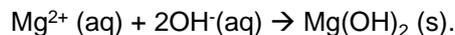$2HCl$ (aq) + $Mg(OH)_2$ (aq) → $MgCl_2$ (aq) + $2H_2O$ (l)

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 $Mg(OH)_2$ (s)

$$Mg^{2+} (aq) + 2OH^- (aq) → Mg(OH)_2 (s).$$

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.

$Mg(OH)_2$ + $2HCl$ → $MgCl_2$ + $2H_2O$
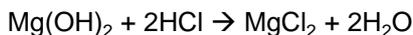
It is safe to use because it so weakly alkaline. It is preferable to using calcium carbonate as it will not produce carbon dioxide gas.

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.

$Ca(OH)_{2 (aq)}$ + $CO_{2 (g)}$ → $CaCO_{3 (s)}$ + $H_2O_{(l)}$
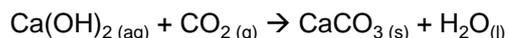
Barium hydroxide would easily dissolve in water. The hydroxide ions present would make the solution strongly alkaline.

$Ba(OH)_{2 (S)}$ + aq → Ba^{2+} (aq) + $2OH^-$ (aq)
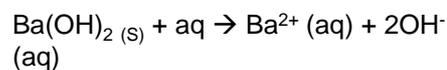
Solubility of Sulphates

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

$BaSO_4$ 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.

Ba + H_2SO_4 → $BaSO_4$ + H_2
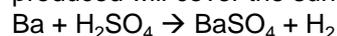
The same effect will happen to a lesser extent with metals going up the group as the solubility increases. The same effect does not happen with other acids like hydrochloric or nitric as they form soluble group 2 salts.

## Thermal decomposition of Group 2 carbonates

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

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

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

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

$Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$
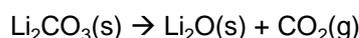
There are a number of experiments that can be done to investigate the ease of decomposition.
One is to heat a known mass of carbonate in a side arm boiling tube and pass the gas produced through lime water. Time for the first permanent cloudiness to appear in the limewater. Repeat for different carbonates 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

lime water
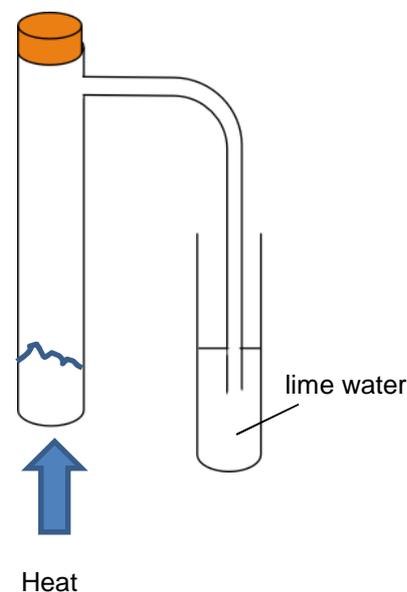
Heat

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 (NO_2) and the White nitrate solid is seen to melt to a colourless solution and then resolidify

$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$

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 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.

$2NaNO_3 \rightarrow 2NaNO_2 + O_2$
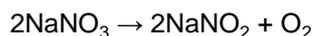
Sodium Nitrate(V)   Sodium Nitrate(III)

Lithium nitrate decomposes in the same way as group 2 nitrates

$4 LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

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

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

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

Titrations

The method for carrying out the titration

- **rinse equipment** (burette with acid, pipette with alkali, conical flask with distilled water)
- **pipette 25 cm^3 of alkali into conical flask**
- **touch surface of alkali with pipette** (to ensure correct amount is added)
- **adds acid solution from burette**
- **make sure the jet space** in the burette **is filled** with acid
- add **a few drops of indicator** and refer to colour change at end point
- phenolphthalein [pink (alkali) to colourless (acid): end point pink colour just disappears] [use if NaOH is used]
- methyl orange [yellow (alkali) to red (acid): end point orange] [use if HCl is used]
- use a white tile underneath the flask to help observe the colour change
- add acid to alkali whilst **swirling the mixture** and **add acid dropwise at end point**
- **note burette reading** before and after addition of acid
- **repeats titration** until **at least 2 concordant results** are obtained- two readings within 0.1 of each other

There will be a small amount of the liquid left in the pipette when it has been emptied. Do not force this out. The pipette is calibrated to allow for it.

If the jet space in the burette is not filled properly prior to commencing the titration it will lead to errors if it then fills during the titration, leading to a larger than expected titre reading.

Working out average titre results
Only make an average of the concordant titre results

Recording results
- Results should be clearly recorded in a table
- Result should be recorded in full (i.e. both initial and final readings)
- **Record titre volumes to 2dp (0.05 cm^3)**

Testing batches
In quality control it will be necessary to do titrations/testing on several samples as the amount/concentration of the chemical being tested may vary between samples.

Safety precautions

Acids and alkalis are corrosive (at low concentrations acids are irritants)
Wear eye protection and gloves
If spilled immediately wash affected parts after spillage

If substance is unknown treat it as potentially toxic and wear gloves.

A conical flask is used in preference to a beaker because it is easier to swirl the mixture in a conical flask without spilling the contents.

Distilled water can be added to the conical flask during a titration to wash the sides of the flask so that all the acid on the side is washed into the reaction mixture to react with the alkali. It does not affect the titration reading as water does not react with the reagents or change the number of moles of acid added.

Only distilled water should be used to wash out conical flasks between titrations because it does not add and extra moles of reagents

If **2 or 3 values are within 0.10cm^3** and therefore **concordant** or close then we can say results are accurate and **reproducible** and **the titration technique is good/ consistent**

Titrating mixtures
If titrating a mixture to work out the concentration of an active ingredient it is necessary to consider if the mixture contains other substances that have acid base properties.
If they don't have acid base properties we can titrate with confidence.

Errors

Calculating apparatus errors
Each type of apparatus has a sensitivity error

- balance $\pm$ 0.001 g
- volumetric flask $\pm$ 0.1 cm^3
- 25 cm^3 pipette $\pm$ 0.1 cm^3
- burette $\pm$ 0.05 cm^3

Calculate the percentage error for each piece of equipment used by

$$\% \text{ error} = \pm \frac{\text{sensitivity error}}{\text{Measurement made on apparatus}} \times 100$$

e.g. for pipette
% error = 0.05/ 25 x100

To calculate the maximum percentage apparatus error in the final result add all the individual equipment errors together.

To decrease the apparatus errors you can either decrease the sensitivity error by using apparatus with a greater resolution (finer scale divisions) or you can increase the size of the measurement made.

If looking at a series of measurements in an investigation the experiments with the smallest readings will have the highest experimental errors.

If the burette used in the titration had an uncertainty for each reading of +/– 0.05 cm^3 then during a titration two reading would be taken so the error on the titre volume would be +/– 0.10 cm^3

Reducing errors in a titration

Replacing measuring cylinders with pipettes or burettes which have lower apparatus sensitivity error will lower the error

To reduce the error in a burette reading it is necessary to make the titre a larger volume. This could be done by: increasing the volume and concentration of the substance in the conical flask or by decreasing the concentration of the substance in the burette.

Reducing errors in measuring mass
Using a more accurate balance or a larger mass will reduce the error in weighing a solid
Weighing sample before and after addition and then calculating difference will ensure a more accurate measurement of the mass added.

Calculating the percentage difference between the actual value and the calculated value

If we calculated an Mr of 203 and the real value is 214, then the calculation is as follows:
Calculate difference 214-203 = 11
% = 11/214 x100
    =5.41%

If the %error due to the apparatus **<** percentage difference between the actual value and the calculated value then there is a discrepancy in the result due to other errors.

If the %error due to the apparatus **>** percentage difference between the actual value and the calculated value then there is no discrepancy and all errors in the results can be explained by the sensitivity of the equipment.

Example 1: 23.6cm³ of H_2SO_4 neutralised 25.0cm³ of 0.15M NaOH. What is the concentration of the H_2SO_4?

H_2SO_4 + 2NaOH → Na_2SO_4 +2H_2O

Step 1: work out amount, in mol, of sodium hydroxide

amount = conc x vol

= 0.15 x 0.025

= 0. 00375 mol

Step 2: use balanced equation to give moles of H_2SO_4

2 moles NaOH : 1 moles H_2SO_4

So 0.00375 NaOH : 0.001875 moles H_2SO_4

Step 3 work out concentration of H_2SO_4

conc= amount/Volume

= 0.001875 / 0.0236

= 0.0794 mol dm⁻³

Example 2: A 25cm³ sample of vinegar was diluted in a 250cm³ volumetric flask. This was then put in a burette and 23.10cm³ of the diluted vinegar neutralised 25 cm³ of 0.1 M NaOH. What is the concentration of the vinegar in gdm⁻³ ?

CH_3CO_2H + NaOH → $CH_3CO_2^-Na^+$ + H_2O

Step 1: work out amount, in mol, of sodium hydroxide

amount = conc x vol

= 0.10 x 0.025

= 0. 00250 mol

Step 2: use balanced equation to give moles of CH_3CO_2H

1 moles NaOH : 1 moles CH_3CO_2H

So 0.00250 NaOH : 0.00250 moles CH_3CO_2H

Step 3 work out concentration of diluted CH_3CO_2H in 23.1 (and 250 cm³)in moldm⁻³

conc= amount/Volume

= 0.00250 / 0.0231

= 0.108 mol dm⁻³

Step 4 work out concentration of original concentrated CH_3CO_2H in 25cm³ in moldm⁻³
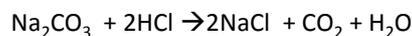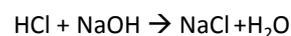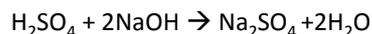
conc = 0.108 x 10 = 1.08 mol dm⁻³

Step 5 work out concentration of CH_3CO_2H in original concentrated 25 cm³ in gdm⁻³

conc in gdm⁻³ = conc in mol dm⁻³ x Mr

= 1.08 x 60 = 64.8 g dm⁻³

To turn concentration measured in mol dm⁻³ into concentration measured in g dm⁻³ multiply by Mr of the substance

conc in g dm⁻³ = conc in mol dm⁻³ x Mr

The concentration in g dm⁻³ is the same as the mass of solute dissolved in 1dm³

Common Titration Equations

CH_3CO_2H + NaOH → $CH_3CO_2^-Na^+$ + H_2O

H_2SO_4 + 2NaOH → Na_2SO_4 +2H_2O

HCl + NaOH → NaCl +H_2O

$NaHCO_3$ + HCl → NaCl + CO_2 + H_2O

Na_2CO_3 + 2HCl →2NaCl + CO_2 + H_2O
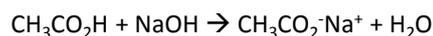
Example 3

950 mg of impure calcium carbonate tablet was crushed. 50.0 cm³ of 1.00 mol dm⁻³ hydrochloric acid, an excess, was then added and the mixture was transferred to a volumetric flask. The volume was made up to exactly 100 cm³ with distilled water. 10.0 cm³ of this solution was titrated with 11.1cm³ of 0.300 mol dm⁻³ sodium hydroxide solution.

What is the percentage of $CaCO_3$ by mass in the tablet

1. Calculate the number of moles of sodium hydroxide used

amount = conc x vol

= 0.30 x 0.0111

= 0. 00333 mol

2. Work out number of moles of hydrochloric acid left in 10.0 cm³

use balanced equation to give moles of HCl

1 mol NaOH : 1 mol HCl

So 0.00333 NaOH : 0.00333 moles HCl

3. Calculate the number of moles of hydrochloric acid left in 100 cm³ of solution

Moles in 100cm³ = 0.00333 x10

=0.0333

4. Calculate the number of moles of HCl that reacted with the indigestion tablet.

In original HCl 50.0 cm³ of 1.00 mol dm⁻³ there is 0.05moles

moles of HCl that reacted with the indigestion tablet.
= 0.05 -0.0333
=0.0167

5 Use balanced equation to give moles of $CaCO_3$

$CaCO_3(s)$ + 2HCl(aq) → $CaCl_2(aq)$ + $CO_2(g)$ + $H_2O(l)$
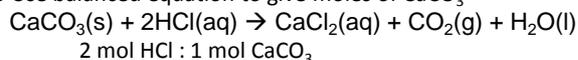
2 mol HCl : 1 mol $CaCO_3$

So 0.0167 HCl : 0.00835 moles $CaCO_3$

6. work out the mass of $CaCO_3$ in original tablet

mass= amout x Mr

= 0.00835 x 100 = 0.835 g

percentage of $CaCO_3$ by mass in the tablet
= 0.835/0.950 x100

= 87.9 %

Making a solution from a solid

•Weigh required mass of solute in a weighing bottle.

• Tip contents into a beaker and add100cm^3 of distilled water. Use a glass rod to stir to help dissolve the solid.

•Sometimes the substance may not dissolve well in cold water so the beaker and its contents could be heated gently until all the solid had dissolved.

•Pour solution into a 250cm^3 graduated flask via a funnel. Rinse beaker and funnel and add washings from the beaker and glass rod to the volumetric flask.
•make up to the mark with distilled water using a dropping pipette for last few drops.
• Invert flask several times to ensure uniform solution.

Weighing can be made more accurate by weighing bottle again after it has been emptied into the beaker- or alternatively the weighing bottle could be washed and washings added to the beaker.
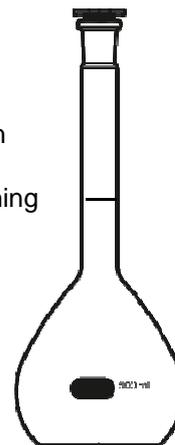
Remember to fill so the bottom of the meniscus sits on the line on the neck of the flask. With dark liquids like potassium manganate it can be difficult to see the meniscus.

Diluting a solution

•Pippette 25cm^3 of original solution into volumetric flask
•make up to the mark with distilled water using a dropping pipette for last few drops.
• Invert flask several times to ensure uniform solution.

Shake the volumetric flask thoroughly to ensure a uniform concentration

Using a pipette is more accurate than a measuring cylinder because it has a smaller sensitivity error

Use a teat pipette to make up to the mark in volumetric flask to ensure volume of solution accurately measured and one doesn't go over the line

Halogens

Fluorine (F_2): very pale yellow gas. It is highly reactive
Chlorine : (Cl_2) greenish, reactive gas, poisonous in high concentrations
Bromine (Br_2) : red liquid, that gives off dense brown/orange poisonous fumes
Iodine (I_2) : 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 van der waals 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

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
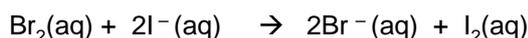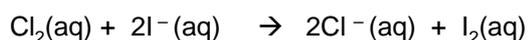
know these observations !

	Chlorine (aq)	Bromine (aq)	Iodine (aq)
potassium chloride (aq)	*Very pale green solution, no reaction*	*Yellow solution, no reaction*	*Brown solution, no reaction*
potassium bromide (aq)	Yellow solution, Cl has displaced Br	*Yellow solution, no reaction*	*Brown solution, no reaction*
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

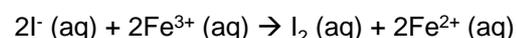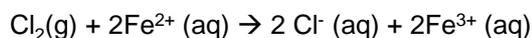|	Chlorine (aq)	Bromine (aq)	Iodine (aq)
potassium chloride (aq)	colourless, no reaction	yellow, no reaction	purple, no reaction
potassium bromide (aq)	yellow, Cl has displaced Br	yellow, no reaction	purple, no reaction
potassium iodide (aq)	purple, Cl has displaced I	purple, Br has displaced I	purple,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

$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$

$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$

The oxidation reactions of metals and metal ion by halogens.

$3Cl_2(g) + 2 Fe (s) \rightarrow 2 FeCl_3 (s)$ $Br_2(l) + 2Na (s) \rightarrow 2NaBr (s)$

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

$Cl_2(g) + 2Fe^{2+} (aq) \rightarrow 2 Cl^- (aq) + 2Fe^{3+} (aq)$

$2I^- (aq) + 2Fe^{3+} (aq) \rightarrow I_2 (aq) + 2Fe^{2+} (aq)$

Chlorine and Bromine can oxidise Fe^{2+} to 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:
$Cl_2(aq) + H_2O(l) \rightarrow HClO(aq) + HCl (aq)$

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 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.
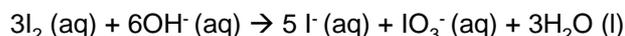
Reaction of halogens with cold dilute NaOH solution:

Cl_2, Br_2, and I_2 in aqueous solutions will react with cold sodium hydroxide. The colour of the halogen solution will fade to colourless

$Cl_2(aq) + 2NaOH(aq) \rightarrow NaCl (aq) + NaClO (aq) + H_2O(l)$

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.

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

$3I_2 (aq) + 6KOH (aq) \rightarrow 5 KI (aq) + KIO_3 (aq) + 3H_2O (l)$

$3I_2 (aq) + 6OH^- (aq) \rightarrow 5 I^- (aq) + IO_3^- (aq) + 3H_2O (l)$

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.
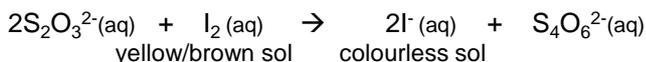
NaClO: sodium chlorate(I)
$NaClO_3$: sodium chlorate(V)
K_2SO_4 potassium sulfate(VI)
K_2SO_3 potassium sulfate(IV)

Thiosulphate redox titration
The redox titration between I_2 and thiosulphate $S_2O_3^{2-}$ is a common exercise.

$2S_2O_3^{2-}(aq) + I_2 (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-}(aq)$
        yellow/brown sol   colourless sol

A starch indicator is added near the end point when the iodine fades a pale yellow to emphasise it.
With starch added the colour change is from blue/black to colourless

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 H_2SO_4 is not strong enough an oxidising reagent to oxidise the chloride and fluoride ions. No redox reactions occur. Only acid-base reactions occur.

$NaF(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HF(g)$
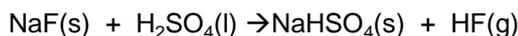
Observations: White steamy fumes of HF are evolved.
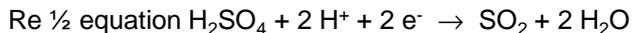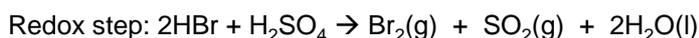
$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$
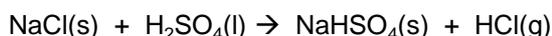
Observations: White steamy fumes of HCl are evolved.

These are acid –base reactions and not redox reactions. H_2SO_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 H_2SO_4 from +6 to + 4 in SO_2

Acid- base step: $NaBr(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HBr(g)$

Redox step: $2HBr + H_2SO_4 \rightarrow Br_2(g) + SO_2(g) + 2H_2O(l)$

Ox ½ equation $2Br^- \rightarrow Br_2 + 2e^-$

Re ½ equation $H_2SO_4 + 2 H^+ + 2 e^- \rightarrow SO_2 + 2 H_2O$
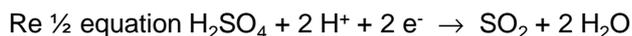
Observations: White steamy fumes of HBr are evolved.
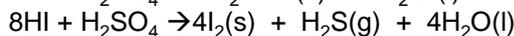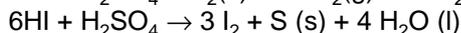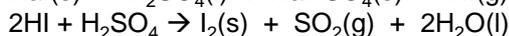
Red fumes of Bromine are also evolved and a colourless, acidic gas SO_2

Reduction product = sulphur dioxide

Note the H_2SO_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 H_2SO_4 to + 4 in SO_2, to 0 in S and -2 in H_2S.

$NaI(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HI(g)$
$2HI + H_2SO_4 \rightarrow I_2(s) + SO_2(g) + 2H_2O(l)$
$6HI + H_2SO_4 \rightarrow 3 I_2 + S (s) + 4 H_2O (l)$
$8HI + H_2SO_4 \rightarrow 4I_2(s) + H_2S(g) + 4H_2O(l)$
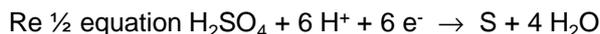
Observations:
White **steamy fumes** of HI are evolved.
Black solid and **purple fumes** of Iodine are also evolved
A **colourless**, acidic **gas** SO_2
A **yellow solid** of Sulphur
H_2S (Hydrogen Sulphide), a **gas** with a **bad egg smell**,

Ox ½ equation $2I^- \rightarrow I_2 + 2e^-$

Re ½ equation $H_2SO_4 + 2 H^+ + 2 e^- \rightarrow SO_2 + 2 H_2O$

Re ½ equation $H_2SO_4 + 6 H^+ + 6 e^- \rightarrow S + 4 H_2O$

Re ½ equation $H_2SO_4 + 8 H^+ + 8 e^- \rightarrow H_2S + 4 H_2O$

Reduction products = sulphur dioxide, sulphur and hydrogen sulphide

Note the H_2SO_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
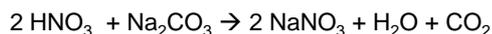
The reactions of halide ions with silver nitrate.

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 Ag_2CO_3. This would mask the desired observations

$2 HNO_3 + Na_2CO_3 \rightarrow 2 NaNO_3 + H_2O + CO_2$

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

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:
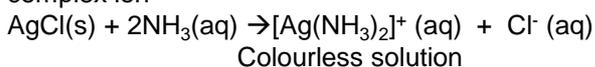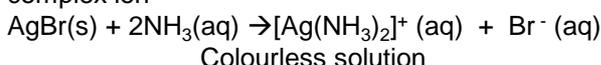
Effect Of Light on Silver Halides

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
$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+ (aq) + Cl^- (aq)$
                    Colourless solution
Silver bromide dissolves in **concentrated ammonia** to form a complex ion
$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+ (aq) + Br^- (aq)$
                    Colourless solution
**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

$NaCl(s) + H_3PO_4(l) \rightarrow NaH_2PO_4(s) + HCl(g)$
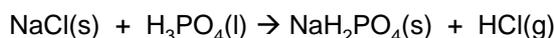
Observations: White steamy fumes of the Hydrogen Halides are evolved.

The Steamy fumes of HCl are produced when the HCl meets the air because it dissolves in the moisture in the air
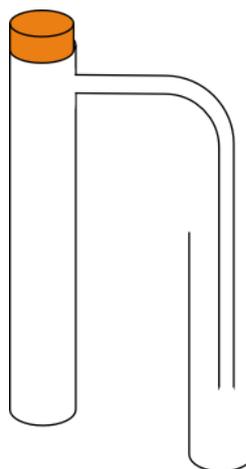
This is the apparatus used to make the hydrogen halide using phosphoric acid.

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.

Hydrogen Halide

The water quickly rises up the tube
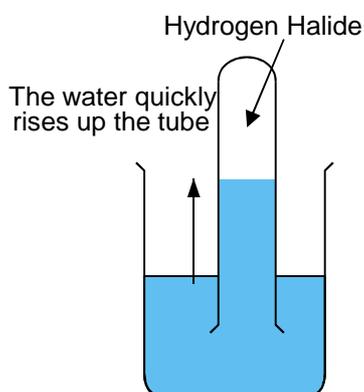
All the hydrogen halides react readily with ammonia to give the **white smoke** of the ammonium halide

$HCl(g) + NH_3 (g) \rightarrow NH_4Cl (s)$
$HBr(g) + NH_3 (g) \rightarrow NH_4Br (s)$
$HI(g) + NH_3 (g) \rightarrow NH_4I (s)$
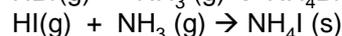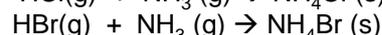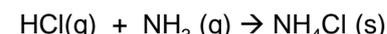
This can be used as a test for the presence of hydrogen halides