

2.3 Group 7 – The Halogens

Physical properties of the Halogens:

- The melting and boiling point of the halogens increases with atomic number due to increased van der Waals (from increased number of electrons).
- This can be seen by their physical states at room temperature.
- Iodine sublimes to a purple vapour.



F_2		Gas	Boiling point increases down the group
Cl_2		Gas	
Br_2		Liquid	
I_2		Solid	
At_2		Solid	

Atomic radius – Increases down the Group:

- **Shells:** More electron shells
- **Shielding:** More shielding (more inner shells)

Ionic radius – Larger than atomic radius:

- **1e added to shell:** More electrons being attracted by same number of protons

First ionisation - Decreases down the Group:

Number of shells increases Shielding increases Atomic radius increases First ionisation energy decreases		<ul style="list-style-type: none"> • Shells: More electron shells • Shielding: More shielding (more inner shells) • No. Protons: Number of protons increases but is outweighed by shells and shielding • Attraction: Therefore attraction is less • Energy: Energy required to remove an electron decreases
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Reactivity – Decreases down the Group:




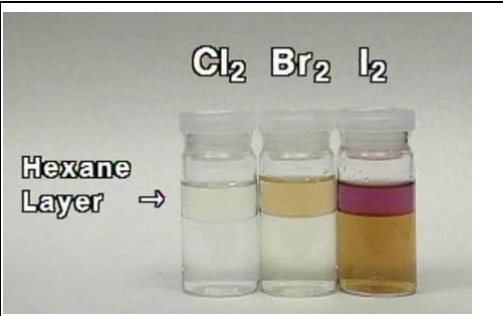
- All gain 1 electrons forming a 1- ion when they react.
- More shells
- More shielding
- Increase in number of protons is outweighed by shells and shielding
- Attraction to capture an electrons decreases down the Group
- Reactivity decreases as you go down the group

Trend in electronegativity decreases down the Group:

- Down the group there are more shells which outweigh the increase in number of protons.
- This reduces the halogen's ability to attract bonding pairs of electrons towards itself

Appearance and solubility of the Halogens

- The halogens are sparingly soluble in water – VDW vs H bonding.
- As you go down the group they become less soluble (as VDW increases).
- They are however soluble in non - polar solvents such as cyclohexane – VDW vs VDW.
- The colours when dissolved in water and a non - polar solvent are shown below:

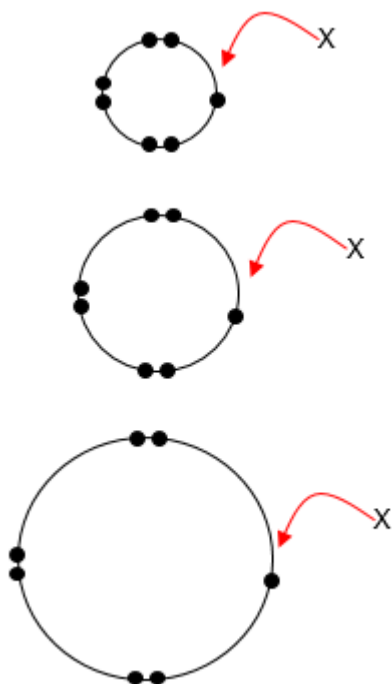
		Halogen	In water	In cyclohexane
		Cl₂	Pale green	Pale Green
		Br₂	Orange	Orange
		I₂	Brown	Violet

Halogens as oxidising agents:



- **Gain of electrons is Reduction**
- This means that whatever they react with must **lose electrons** and be **Oxidised**
- This makes the **Halogens** good **Oxidising agents**
- **Reactivity decreases** as you go **down the Group**.
- This means they **gain their electrons less readily**.
- This means as you go **down Group 7**, their **oxidising power decreases**.

Explanation:



- All gain 1 electrons forming a 1- ion when they react.
- **More shells**
- **More shielding**
- **Increase in number of protons is outweighed by shells and shielding**
- **Attraction to capture an electrons decreases down the Group**
- **Reactivity decreases** as you go **down the group**
- **The power of the Oxidising agent decreases** as you go **down the group**

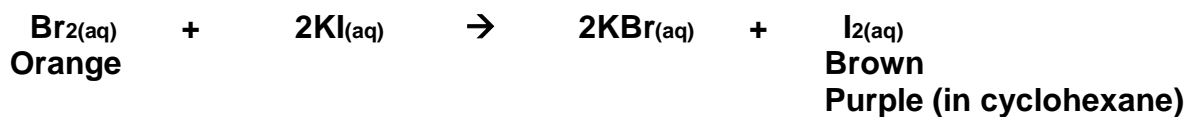
Displacement reactions of the halogens:

- Redox reactions show the Halogens ability to form ions reduces as you go down the Group.
- By competing the Halogens (Cl_2 , Br_2 , and I_2) with the Halides (Cl^- , Br^- , and I^-)
- Each Halogen is mixed with each of the Halides.
- The more reactive Halogen will oxidise and displace the Halide of a less reactive Halogen.
- Halogens are coloured in solution and in a hydrocarbon solvent such as cyclohexane.
- This can indicate whether a redox reaction has occurred:

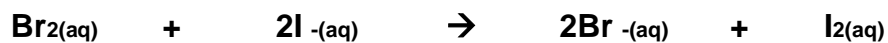
	Cl₂(aq)	Br₂(aq)	I₂(aq)
Cl₂(aq)		Orange	Brown
Add cyclohexane		Dark orange	Purple
Br₂(aq)	No reaction		Brown
Add cyclohexane	Stays orange / dark orange		Purple
I₂(aq)	No reaction	No reaction	
Add cyclohexane	Stays brown / purple	Stays Brown / purple	

3) Bromine and Potassium iodide:

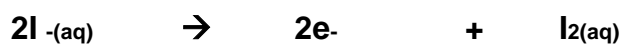
Full equation and colours:



Ionic equation:



Half equations:



Explanation:

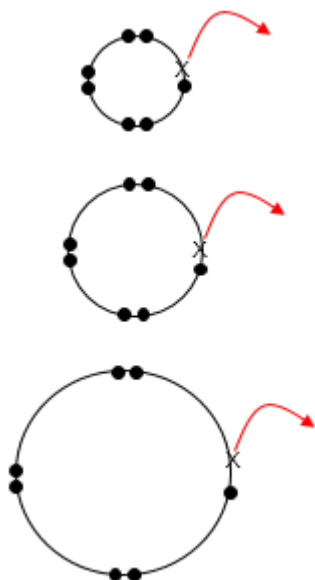
Bromine is further up the Group than Iodine so is a stronger oxidising agent, so accepts electrons more readily than Iodine

Halides as reducing agents:



- **Loss of electrons is Oxidation**
- This means that whatever they react with must **gain electrons** and be **Reduced**
- This makes the **Halides** good **Reducing agents**
- As you go down the Group, **electrons are lost more readily**.
- This means as you go **down Group 7**, their **reducing power increases**.

Explanation:



- All lose 1 electron forming a halogen when they react.
- **More shells**
- **More shielding**
- Increase in number of protons is outweighed by shells and shielding
- Attraction to decreases down the Group
- Reactivity increases down the group
- The power of the Reducing agent increases as you go down the group

Reactions of the Halides, X⁻ with concentrated sulphuric acid, H₂SO₄

Reduction products of Sulphuric acid, H₂SO₄:

Name	Sulphuric acid	Sulphur dioxide	Sulphur	Hydrogen sulphate
Formula	H ₂ SO ₄	SO ₂	S	H ₂ S
Oxidation number	+6	+4	0	-2
Test for sulphur product	White fumes (with NH ₃ gas) / Damp blue litmus paper turns red	Dichromate paper turns orange → green Choking smell	Yellow solid	Lead ethanoate paper turns black Bad egg smell
As the power of the Reducing agent increases				
H ₂ SO ₄ becomes more reduced - Therefore the halide must be oxidised to the halogen				
How far	F ⁻ and Cl ⁻	Br ⁻ and I ⁻		I ⁻

The Experiment: Reactions of the Halide ions, X⁻ with Sulphuric acid, H₂SO₄

- Add 0.1g of the solid halide (eg KCl) to a test tube.
- Add 10 drops of concentrated sulphuric acid, H₂SO₄ and warm if necessary.

Observations:

<i>Solid halide</i>	<i>Observations</i>	<i>Further observations</i>
<i>KCl</i>	White fumes	No further reaction
<i>KBr</i>	White fumes	Brown fumes (Br ₂) and SO ₂ (choking smell)
<i>KI</i>	White fumes	Purple fumes (I ₂), SO ₂ (choking smell), S and H ₂ S (bad egg smell)

Equations:

1) With KCl / Cl⁻ / Chloride ion



Cl⁻ cannot reduce H₂SO₄, it is not a strong enough reducing agent

2) With KBr / Br⁻ / Bromide ion



Br⁻ can reduce H₂SO₄ to SO₂ but no further as it is a stronger reducing agent:

Half equations: Construct and balance using electrons:



Overall:



3) With KI / I- / Iodide ion

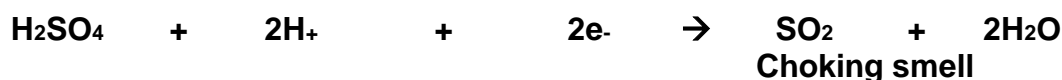


I- can reduce H₂SO₄ to SO₂ / S / H₂S as it is the strongest reducing agent

This happens in 3 simultaneous reactions:

a) To make SO₂:

Half equations: Construct and balance using electrons:



Overall:



b) To make S:

Half equations: Construct and balance using electrons:

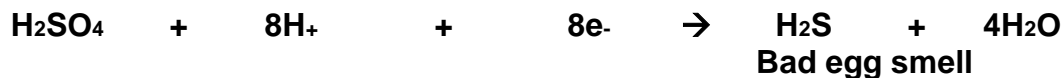


Overall:



c) To make H₂S:

Half equations: Construct and balance using electrons:



Overall:

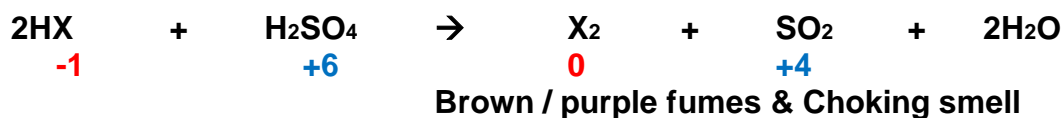


Summary of the reduction reactions of the Halides:

1) All Halides do the following – H₂SO₄ is **not reduced**:



2) The HX – Bromide and Iodide will reduce H₂SO₄ to SO₂



3) The HX –Iodide will also reduce H₂SO₄ to H₂S (and S)

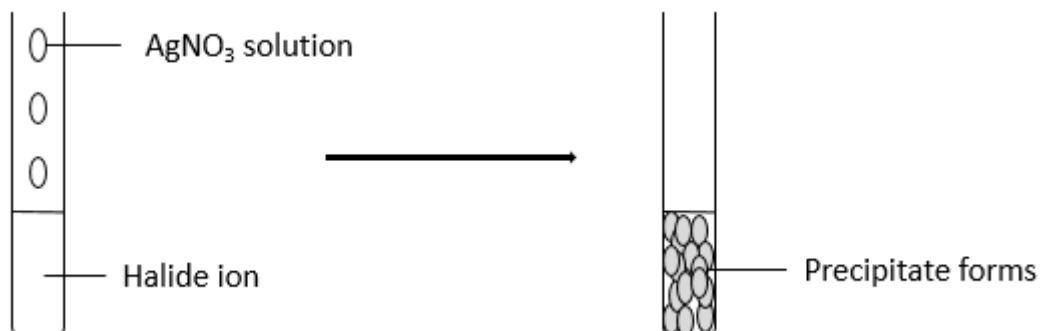


Summary of Oxidation / Reduction of the Halogens and the Halides

Halogens			Halides		
F ₂	↑	Oxidising strength increases up Group: Electrons are gained more readily	F ⁻	↓	Reducing strength increases down Group: Electrons are lost more readily
Cl ₂			Cl ⁻		
Br ₂			Br ⁻		
I ₂			I ⁻		

Testing for Halide ions – (Part of Required Practical 4)

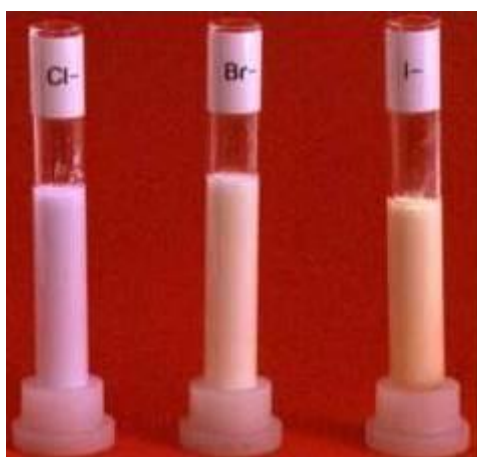
- Dissolve a small amount of Halide compound in water
- Add **nitric acid** to **remove any other ions** that may interfere with the test such as carbonates.
- Add a few drops of silver nitrate, **AgNO₃**.
- The silver ions, Ag⁺ combines with the Halide ions, X⁻ to **form a silver halide precipitate**
- The silver halide precipitates are coloured depending upon the halide present:



- **Sometimes it is difficult to judge the exact colour.**
- **Ammonia can be added** as the different silver halides as they have different solubility's in ammonia.
- **The solubility of the precipitates decreases down the group.**

Results:

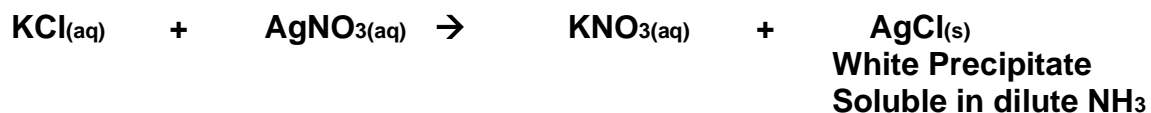
Halide ion	Observations	With Ammonia	Solubility of the precipitate
Cl⁻	White precipitate	Dissolves in dilute NH ₃ solution	Most soluble
Br⁻	Cream precipitate	Dissolves in concentrated NH ₃ solution	
I⁻	Yellow precipitate	Insoluble	Least soluble



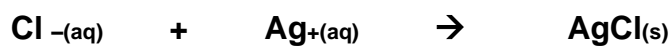
Equations:

1) Potassium Chloride + Silver nitrate

Full:



Ionic:

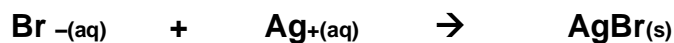


2) Potassium Bromide + Silver nitrate

Full:



Ionic:

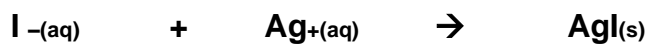


3) Potassium Iodide + Silver nitrate

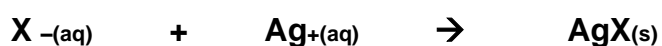
Full:



Ionic:



Generally:



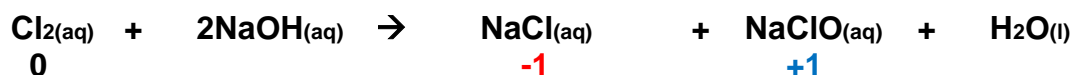
Disproportionation reactions – Uses of chlorine and Chlorate (I)

Disproportionation

Disproportionation:

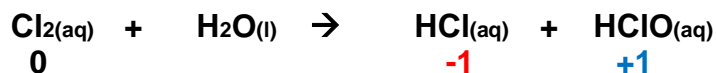
Is a REDOX reaction where the same element has been both Oxidised and Reduced

1) Chlorine and cold NaOH – Bleach:

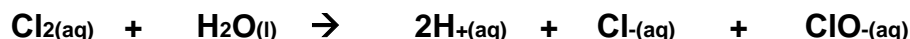


- The Cl has been oxidised and reduced in this reaction.
- Sodium chlorate (I) is used in bleach.
- Uses – bleaching paper / textiles / cleaning toilets

2) Chlorine and drinking water:



Or dissociated:



- In this reaction, the Cl has been oxidised and reduced too.
- The chlorate (I) ion kills bacteria.
- Chlorine reacts with organic compounds from plant decomposition to form chlorinated compounds – carcinogenic.
- Chlorine is toxic.
- Risk and Benefit must be assessed when making decisions on this scale.

Further reactions - In sunlight HClO decomposes further:



Or dissociated:



- Combining these 2 reactions gives:



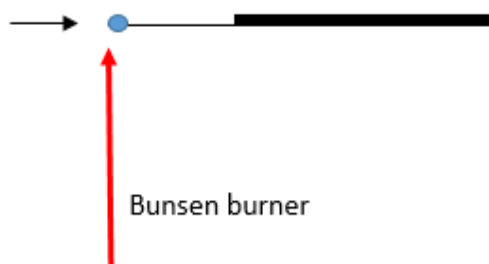
- This means that the reaction between chlorine and water **in sunlight** produces hydrochloric acid and oxygen:

Required Practical 4 – Test for ions

Positive ions:

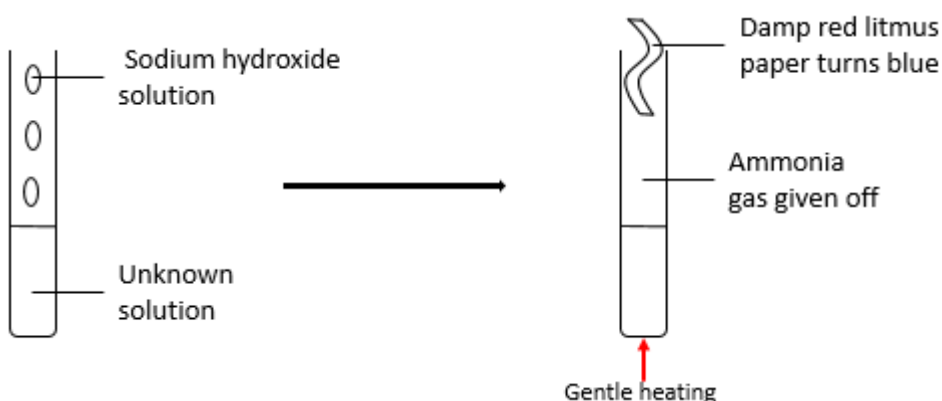
1) Test for Group 2 metal ions, M_{2+} - Flame tests

Nichrome wire dipped in concentrated HCl (to clean) then the unknown compound



Metal ion	Flame colour
Calcium, Ca_{2+}	Brick red
Strontium, Sr_{2+}	Red
Barium, Ba_{2+}	Pale green

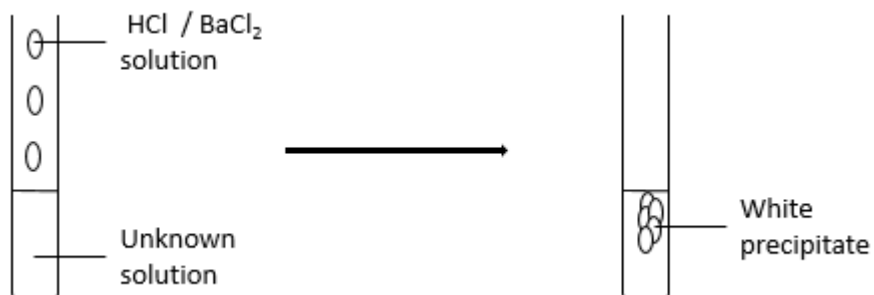
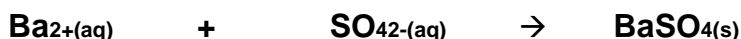
2) Test for ammonium ions, NH_4^+ :



- With sodium hydroxide and heat, ammonia gas is given off.
- Litmus paper must be damp for ammonia gas to dissolve in.
- **Turns Blue**

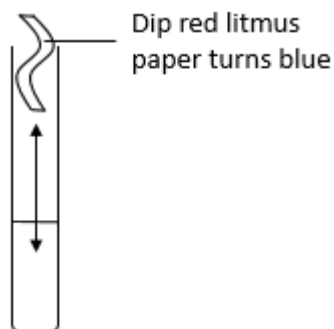
Negative ions:

3) Test for sulphate ions, SO_4^{2-}



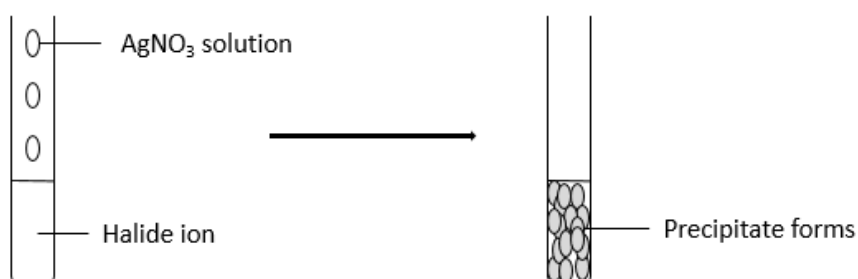
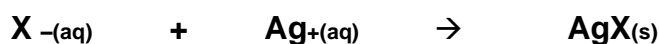
- Add **HCl** first – This removes any sulphites or carbonates that may also give a white precipitate.
- Add **BaCl₂** solution: **White precipitate of BaSO₄** will form.

4) Test for hydroxide ions, OH-



- Dip red litmus paper onto the solution.
- If it turns blue, hydroxide, OH⁻ are present.

5) Testing for Halide ions, X-



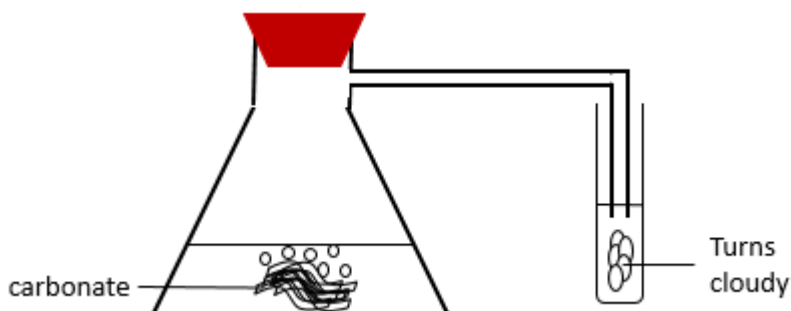
- Add **nitric acid** to **remove any other ions** that may interfere with the test.
- Add silver nitrate, **AgNO₃**.
- The silver ions, Ag⁺ combines with the Halide ions, X⁻ to **form a silver halide precipitate**

- **Ammonia can be added** as the different silver halides as they have different solubility's in ammonia.

Results:

Halide ion	Observations	With Ammonia	Solubility of the precipitate
Cl ⁻	White precipitate	Dissolves in dilute NH ₃ solution	Most soluble
Br ⁻	Cream precipitate	Dissolves in concentrated NH ₃ solution	
I ⁻	Yellow precipitate	Insoluble	Least soluble

6) Testing for carbonate ions, CO₃²⁻



- Add **hydrochloric acid**.
- It will fizz if carbonate present, **CO₃²⁻**.
- **CO₂** gas is made.
- **CO₂** will turn **limewater cloudy**.