

2.3 Halogens

Fluorine (F₂): very pale yellow gas. It is highly reactive
 Chlorine : (Cl₂) greenish, reactive gas, poisonous in high concentrations
 Bromine (Br₂) : red liquid, that gives off dense brown/orange poisonous fumes
 Iodine (I₂) : 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.

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.

1. The displacement 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.

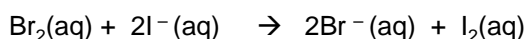
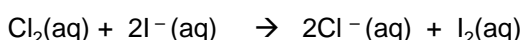
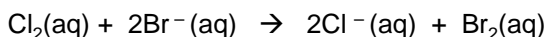
The oxidising strength decreases down the group. Oxidising agents are electron acceptors.

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

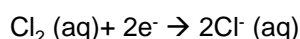
know these observations !

	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)



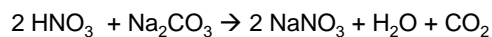
Be able to write these reactions as two half equations showing oxidation or reduction
 e.g. $2\text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{e}^-$



2. The reactions of halide ions with silver nitrate.

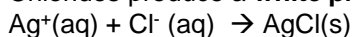
This reaction is used as a test to identify which halide ion is present. The test solution is made acidic with **nitric acid**, and then **silver nitrate solution** is added dropwise.

The role of nitric acid is to react with any carbonates present to prevent formation of the precipitate Ag₂CO₃. This would mask the desired observations

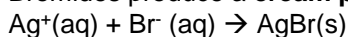


Fluorides produce no precipitate

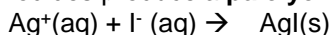
Chlorides produce a **white precipitate**



Bromides produce a **cream precipitate**

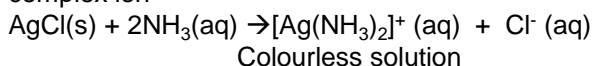


Iodides produce a **pale yellow precipitate**

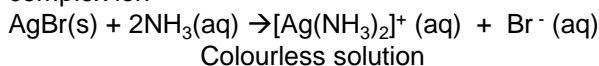


The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:

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.

3. The reaction of halide salts with concentrated sulfuric 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 sulfuric acid.

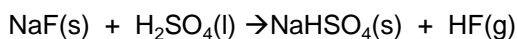
Know the equations and observations of these reactions very well.

Explanation of differing reducing power of halides

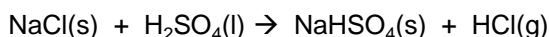
A reducing agent donates electrons.
The reducing power of the halides increases down group 7
They have a greater tendency to donate electrons.
This is because as the ions get bigger it is easier for the outer electrons to be given away as the pull from the nucleus on them becomes smaller.

Fluoride and Chloride

F⁻ and Cl⁻ ions are not strong enough reducing agents to reduce the S in H₂SO₄.
No redox reactions occur. Only acid-base reactions occur.



Observations: White steamy fumes of HF are evolved.

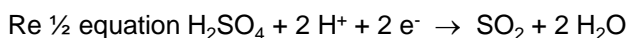
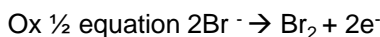
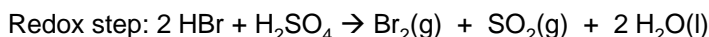


Observations: White steamy fumes of HCl are evolved.

These are acid-base reactions and not redox reactions. H₂SO₄ 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 sulfur in H₂SO₄ from +6 to +4 in SO₂



Observations: White steamy fumes of HBr are evolved.

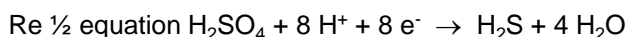
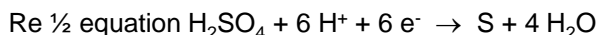
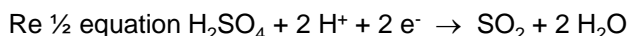
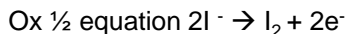
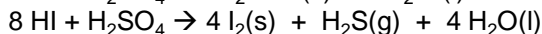
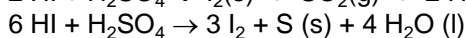
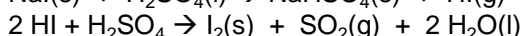
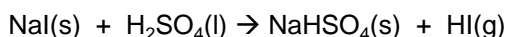
Red fumes of bromine are also evolved and a colourless, acidic gas **SO₂**

Reduction product = sulfur dioxide

Note the H₂SO₄ 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 sulfur from +6 in H₂SO₄ to +4 in SO₂, to 0 in S and -2 in H₂S.



Observations:

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

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

A **colourless**, acidic **gas** SO₂

A **yellow solid** of sulfur

H₂S (Hydrogen sulfide), a **gas** with a **bad egg smell**,

Reduction products = sulfur dioxide, sulfur and hydrogen sulfide

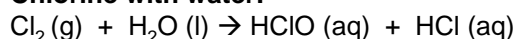
Note the H₂SO₄ plays the role of acid in the first step producing HI and then acts as an oxidising agent in the three redox steps.

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

4. The disproportionation reactions of chlorine.

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

Chlorine with water:

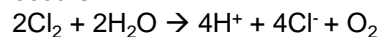


Chlorine is both simultaneously reducing and oxidising

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.

Reaction with water in sunlight

If the chlorine is bubble through water in the **presence of bright sunlight** a different reaction occurs



The same reaction occurs to the equilibrium mixture of chlorine water. The greenish colour of chlorine water fades as the Cl_2 reacts and a colourless gas (O_2) is produced

The 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 chlorine with cold dilute NaOH solution:

Cl_2 , (and Br_2 , 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.

Naming chlorates/sulfates

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)