

# 11 Halogens

All halogens exist as diatomic molecules

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 induced dipole-dipole forces (London forces) between the molecules. As the intermolecular forces get larger more energy has to be put into break these intermolecular forces. This increases the melting and boiling points

## Redox reactions and reactivity of halogens and their compounds

### Electronic configuration.

All group 7 elements have the outer shell s<sup>2</sup>p<sup>5</sup> electron configuration.

The will often react by gaining of one electron in redox reactions to form 1<sup>-</sup> ions

### 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 !

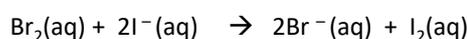
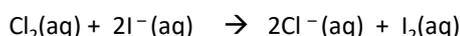
	Chlorine (aq)	Bromine (aq)	Iodine (aq)
potassium chloride (aq)	<i>Very pale green solution, no reaction</i>	<i>Yellow solution, no reaction</i>	<i>Brown solution, no reaction</i>
potassium bromide (aq)	Yellow solution, Cl has displaced Br	<i>Yellow solution, no reaction</i>	<i>Brown solution, no reaction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

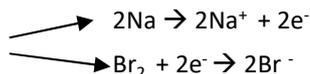
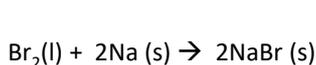
### Observations if an organic solvent is added

	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

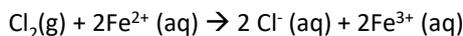
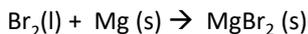
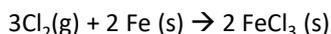
The colour of the organic solvent layer in the test tube shows which free halogen is present in solution.  
Chlorine = colourless  
Bromine = **yellow**  
Iodine = **purple**



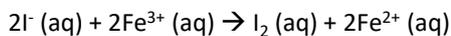
### The oxidation reactions of metals and metal ion by halogens.



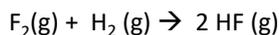
In all reactions where halogens are reacting with metals, the metals are being oxidised



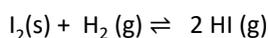
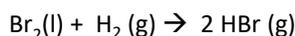
Chlorine and bromine can oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Iodine is not strong enough oxidising agent to do this reaction. The reaction is reversed for iodine



### The reactions of the elements with hydrogen



All the halogens react with hydrogen gas to produce hydrogen halides. The reactions decrease in speed and vigour going down the group



Hydrogen iodide easily converts back into hydrogen and iodine on heating. The general trend is the hydrides **become less stable going down the group**. This can be explained by the decreasing size of the H-Hal bond energy going down the group. This is because as the halogen atoms are get bigger their bond length is longer. The bonding pair of electrons is gets further from the halogen nuclei.

### 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.

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**  
 $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

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



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  
 $\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \rightarrow [\text{Ag}(\text{NH}_3)_2]^+(\text{aq}) + \text{Cl}^-(\text{aq})$   
Colourless solution

**Silver bromide** dissolves in **concentrated ammonia** to form a complex ion  
 $\text{AgBr}(\text{s}) + 2\text{NH}_3(\text{aq}) \rightarrow [\text{Ag}(\text{NH}_3)_2]^+(\text{aq}) + \text{Br}^-(\text{aq})$   
Colourless solution

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

## 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.

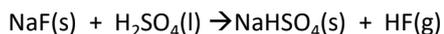
**Know the equations and observations of these reactions very well.**

### Explanation of differing reducing power of halides

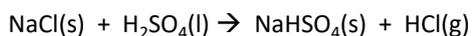
A reducing agent donates electrons.  
The reducing power of the halides increases down group 7  
They have a greater tendency to donate electrons.  
This is because as the ions get bigger it is easier for the outer electrons to be given away as the pull from the nucleus on them becomes smaller.

### Fluoride and Chloride

F<sup>-</sup> and Cl<sup>-</sup> ions are not strong enough reducing agents to reduce the S in H<sub>2</sub>SO<sub>4</sub>. No redox reactions occur. Only acid-base reactions occur.



Observations: White steamy fumes of HF are evolved.

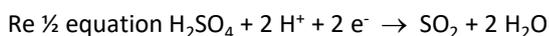
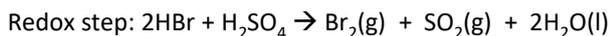


Observations: White steamy fumes of HCl are evolved.

These are acid-base reactions and not redox reactions. H<sub>2</sub>SO<sub>4</sub> plays the role of an acid (proton donor).

### Bromide

Br<sup>-</sup> ions are stronger reducing agents than Cl<sup>-</sup> and F<sup>-</sup> and after the initial acid-base reaction reduce the sulfur in H<sub>2</sub>SO<sub>4</sub> from +6 to +4 in SO<sub>2</sub>



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

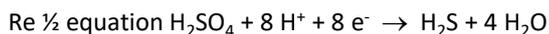
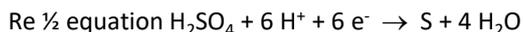
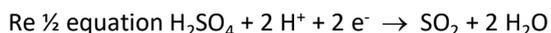
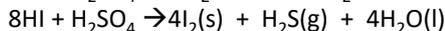
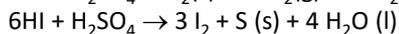
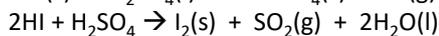
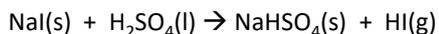
Red fumes of bromine are also evolved and a colourless, acidic gas SO<sub>2</sub>

Reduction product = sulfur dioxide

Note the H<sub>2</sub>SO<sub>4</sub> 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<sup>-</sup> ions are the strongest halide reducing agents. They can reduce the sulfur from +6 in H<sub>2</sub>SO<sub>4</sub> to +4 in SO<sub>2</sub>, to 0 in S and -2 in H<sub>2</sub>S.



### Observations:

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

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

A **colourless, acidic gas** SO<sub>2</sub>

A **yellow solid** of sulfur

**H<sub>2</sub>S** (Hydrogen sulfide), a **gas** with a **bad egg smell**,

Reduction products = sulfur dioxide, sulfur and hydrogen sulfide

Note the H<sub>2</sub>SO<sub>4</sub> 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 and chlorate(I).

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

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

##### 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.

Chlorine is both simultaneously reducing and oxidising

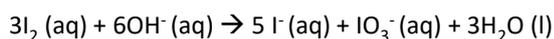
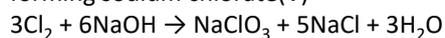
##### Reaction of Chlorine with cold dilute NaOH solution:

$\text{Cl}_2$ , (and  $\text{Br}_2$ ,  $\text{I}_2$ ) 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

If **hot** sodium hydroxide is used a different disproportionation reaction occurs forming sodium chlorate(V)



##### 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.

$\text{NaClO}$ : sodium chlorate(I)

$\text{NaClO}_3$ : sodium chlorate(V)

$\text{K}_2\text{SO}_4$  potassium sulfate(VI)

$\text{K}_2\text{SO}_3$  potassium sulfate(IV)

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.

Chlorine is used to make

- Bleaches (see above)
- PVC (see chapter 15 for description of PVC polymer)
- Halogenated hydrocarbons as solvents, refrigerants and in aerosols. (see chapter 16 for these)