

Group 7

To succeed with this topic, you need to:

- understand terms describing physical properties of chemicals
- understand the use of chemical formulae in balanced equations (see Factsheet 03 Moles and equations)
- understand practical terms such as precipitate, solution and the use of universal indicator
- understand atomic structure (see Factsheet 01 Atomic structure)

After working through this Factsheet, you will be able to:

- recall physical properties of group 7
- recall simple chemical tests for the elements
- recall identification tests for halide ions
- have some understanding of reactions of different halogen compounds
- give examples of disproportionation
- recall the relative oxidising strengths of the elements
- have some understanding of the chlor-alkali industry and the extraction of bromine from sea water

The halogens are the most reactive group of non-metals. They are strong oxidising agents, as they require only 1 electron to complete their octet of electrons.

Trends within the group

- melting /boiling points increase as group is descended
- atomic radii increase as group is descended
- ionic radii increase as group is descended

Note that ionic radii are larger than atomic radii, as in each case an electron is added to the atom to form the -1 halide ion, and repulsions increase as an extra electron is added.

Exam Hint - Questions on the reactions of the halogens and their compounds are popular, as they cover redox reactions, practical tests and industrial chemistry. Do not just learn the equations, but also the context of each chemical reaction.

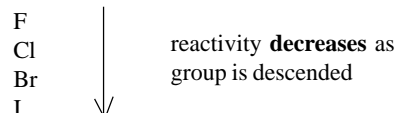
Exam Hint - You do not need to know the actual values of boiling points and atomic/ionic radii, but you must learn the trends they show.

Table 1. The Halogens

Element			State at RTP	Boiling point (°C)	Atomic radius (pm)	Ionic radius (pm)
Symbol	Name	Formula				
F	Fluorine	F ₂	pale yellow gas	-188.0	72	136
Cl	Chlorine	Cl ₂	yellow/green gas	-34.7	99	181
Br	Bromine	Br ₂	brown volatile liquid	58.8	114	195
I	Iodine	I ₂	dark grey shiny solid	184.0	133	216

Reactivity of the Halogens

The halogens do not exist naturally in their elemental form because they are so reactive – very strong oxidising agents.

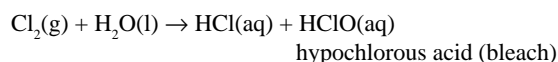


Fluorine is the most reactive as it is the smallest atom. It attracts electrons into a low energy shell which is close to the nucleus with little shielding.

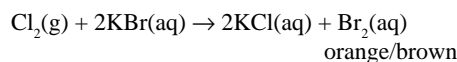
Tests for the halogens

Chlorine – a pungent, yellow/green gas, toxic.

- a) Turns damp litmus paper red, then bleaches it white.



- b) Bubble chlorine gas through colourless potassium bromide solution and bromine (orange/brown) is liberated.



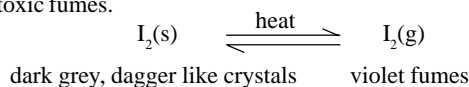
Bromine

A pungent, red/brown volatile liquid, gives off orange/brown toxic fumes in air.

- a) Bromine will bleach damp litmus paper, but much slower than chlorine
b) Add bromine to water, then add a little dilute sodium hydroxide solution. The orange/brown aqueous solution of bromine becomes colourless on addition of the alkali

Iodine

A shiny dark grey solid which **sublimes** on heating, forming pungent, violet toxic fumes.



Iodine turns starch solution from colourless to blue/black

Solubility of the halogens

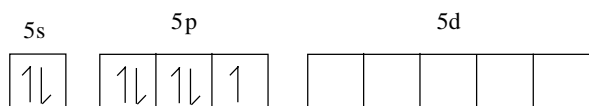
All halogens except fluorine dissolve slightly in water and discolour it. Fluorine is such a powerful oxidising agent that it converts water to oxygen. Solubility decreases down the group.

The range of halogen compounds

The halogens have oxidation numbers (see Factsheet 11) which range from -1 in simple halides to +7 in compounds such as potassium iodate (VII) (KIO_3), though some oxidation states are more common than others.

The halogens are able to have such a wide range of oxidation numbers because they have the ability to "de-pair" some of their electrons, making them available for bonding.

e.g. Iodine



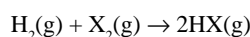
With only one unpaired electron, it can form only one covalent bond (e.g. ICl) But if one electron is promoted to the 5d orbital:



Now with three unpaired electrons, we can form three covalent bonds (e.g. ICl_3), and so on. Note that fluorine cannot do this, as there is no 2d orbital.

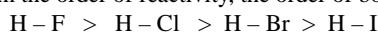
Hydrogen Halides

These are formed by reacting the halogen with hydrogen:



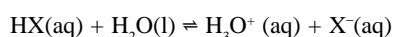
All are colourless gases at room temperature, and give cloudy white fumes in moist air.

As expected from the order of reactivity, the order of bond strengths is:



This is also the order of thermal stability.

The hydrogen halides are covalent substances, but are all highly soluble in water. They are soluble because they are polar, and so dissociate easily in water, acting as proton donors (i.e. acids):



HI has the weakest bond, due to I^- being the largest anion. Therefore HI dissociates the most easily, so HI is the strongest acid.

Acidic strength: $\text{HF} \ll \text{HCl} < \text{HBr} < \text{HI}$

Hydrogen fluoride is a much weaker acid than the rest due to the HF bond being so strong and the presence of hydrogen bonding which discourages dissociation further.

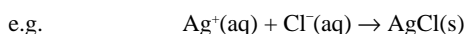
Despite being a weak acid (i.e. donating few H^+ ions into solution) HF is a very corrosive chemical which attacks glass, so solutions of HF are stored in polythene bottles.

Generally the boiling points of hydrogen halides increased down the group, as the increase in size of the molecules leads to increased Van der Waals forces. However, HF is an exception - it has a much higher boiling point than the other hydrogen halides. This is due to hydrogen bonding (see Factsheet 05).

Hydrogen halide	HF	HCl	HBr	HI
Boiling point	+20	-85	-67	-35

The Halides - Oxidation Number -1

All metal halides are soluble in water, except for silver and lead halides. Precipitates of these halides are produced when aqueous solutions of halides are treated with $\text{Ag}^+(\text{aq})$ or $\text{Pb}^{2+}(\text{aq})$



The action of silver nitrate solution followed by ammonia solution (or sunlight) can be used as a test for halide ions (Table 2):

Table 2. Tests for Halide ions

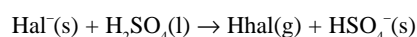
	F^-	Cl^-	Br^-	I^-
Addition of $\text{AgNO}_3(\text{aq})$	No reaction	White precipitate	Cream precipitate	Yellow precipitate
Addition of dilute $\text{NH}_3(\text{aq})$	Soluble	Soluble	insoluble	Insoluble
Addition of conc $\text{NH}_3(\text{aq})$	Soluble	Soluble	Soluble	Insoluble
Effect of sunlight on silver halide	No effect	White \rightarrow purple grey	Cream \rightarrow green/yellow	Remains yellow

Reactions of halide salts with concentrated sulphuric acid

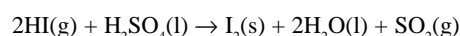
The reaction of each halide salt with concentrated H_2SO_4 varies depending on how easily the halide ion is oxidised.

Due to the size of the anions, I^- is the easiest halide ion to oxidise, and F^- the most difficult, as it is the most stable.

If concentrated sulphuric acid is added to solid halide salts, the first product is the hydrogen halide:



But concentrated sulphuric acid is also an oxidising agent, and is powerful enough to oxidise HBr and HI to Br_2 and I_2 (but does not affect HCl and HF)

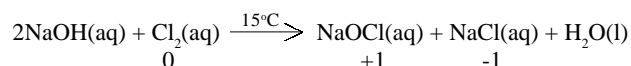


	Solid halide			
	Fluoride	Chloride	Bromide	Iodide
Addition of conc H_2SO_4	HF(g) produced	HCl(g) produced	HBr(g) + $\text{Br}_2(\text{g})$ produced	HI(g) + $\text{I}_2(\text{g})$ produced

Oxidation Number +1 eg sodium chlorate (I), NaClO

The reactions of sodium chlorate (I) are those of an oxidising agent, for example it will oxidise pale green $\text{Fe}^{2+}(\text{aq})$ ions to yellow brown $\text{Fe}^{3+}(\text{aq})$ ions, or $\text{I}^-(\text{aq})$ to $\text{I}_2(\text{aq})$

Sodium chlorate (I) is common household bleach, and is formed from the reaction between chlorine and sodium hydroxide at 15°C



The oxidation state of chlorine has been indicated on the above equation - notice how the element chlorine is simultaneously oxidised and reduced - so has undergone **disproportionation** (Factsheet 11)

