3.1.3 Halogens

All halogens exist as diatomic molecules

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 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^2p^5 electron configuration.
The will often react by gaining of one electron in redox reactions to form 1^- ions

1. The displacement reactions of halide ions by halogens.

A halogen that is more reactive will displace a halogen that has a lower reactivity from one of its compounds

The reactivity of the halogens decreases down the group as the atoms get bigger with more shielding so they less easily attract and accept electrons. They therefore form -1 ions less easily down the group

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**

Explanation of reactivity
Chlorine is more reactive than bromine because it will gain an electron and form a negative ion more easily than bromine. The is because an atom of chlorine is smaller than bromine and the outermost shell of chlorine is less shielded than bromine so the electron to be gained is attracted more strongly to the nucleus in chlorine than bromine.

$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$
$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$
$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$

2. The disproportionation reactions of chlorine.

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

Chlorine with water:
$Cl_2(g) + H_2O(l) \rightarrow HClO(aq) + HCl(aq)$

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.

Chlorine is both simultaneously reducing and oxidising. It changes from 0 in Cl_2 to -1 in HCl and +1 in HClO

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 by its killing of bacteria outweigh its risks of toxic effects and possible risks from formation of chlorinated hydrocarbons .

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 chlorine is reacting by disproportionation. 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 (sodium chlorate (I)) is used as Bleach and to disinfect/ kill bacteria

If the hot sodium hydroxide is used a different disproportionation reaction occurs forming sodium chlorate(V)
$3Cl_2 + 6NaOH \rightarrow NaClO_3 + 5NaCl + 3H_2O$

3. 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 drop wise.

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

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

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
$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$
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.