

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.

Trends in melting point and boiling point

Increase down the group

As the molecules become larger they have more electrons and so have larger London forces between the molecules. As the intermolecular forces get larger, more energy has to be put into overcoming the forces. This increases the melting and boiling points.

Element	Melting Point (°C)	Boiling Point (°C)	Physical State
Fluorine	-220	-188	Gas
Chlorine	-101	-35	Gas
Bromine	-7	59	Liquid
Iodine	+114	184	Solid

Trends 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.

Reactions of halogens

The oxidation 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.

	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)

All the halide salt solutions (KI, NaBr, KCl etc.) are colourless



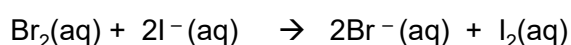
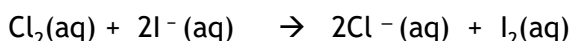
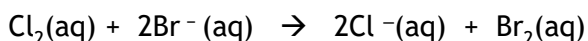
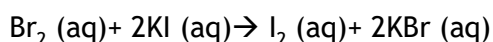
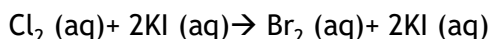
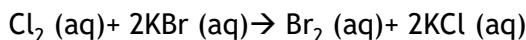
Br₂ (aq)

I₂ (aq)

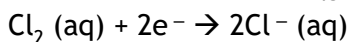
Observations if an organic solvent is added

	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**



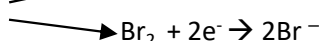
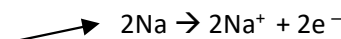
Reduction half equation (gaining electrons)



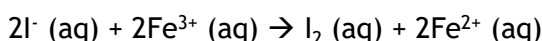
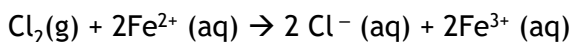
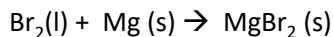
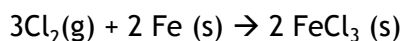
Oxidation half equation (losing electrons)



The oxidation reactions of metals and metal ion by halogens.



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



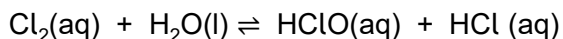
Chlorine and bromine can oxidise Fe^{2+} to Fe^{3+} .

Iodine is not strong enough an oxidising agent to do this reaction. The reaction is reversed for iodine.

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 changing its oxidation number from 0 to -1 and 0 to +1

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.

The pale greenish colour of these solutions is due to the Cl_2

Chlorine is used in water treatment to kill bacteria. Chlorine can be 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 with water in sunlight

If the chlorine is bubbled 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.

Reaction of halogens with cold dilute NaOH solution:

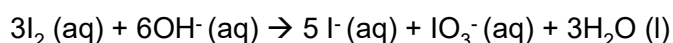
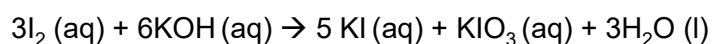
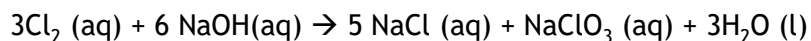
Cl₂, Br₂, and I₂ in aqueous solutions will react with cold sodium hydroxide. The colour of the halogen solution will fade to colourless



The mixture of NaCl and NaClO is used as bleach and to disinfect and kill bacteria.

Reaction of halogens with hot dilute NaOH solution:

With hot alkali disproportionation also occurs but the halogen that is oxidised goes to a higher oxidation state.



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)

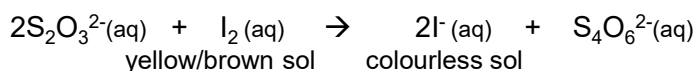
NaClO₃: sodium chlorate(V)

K₂SO₄: potassium sulfate(VI)

K₂SO₃: potassium sulfate(IV)

Thiosulfate redox titration

The redox titration between I₂ and thiosulfate S₂O₃²⁻ is a common exercise.



A starch indicator is added near the end point when the iodine fades a pale yellow to emphasise it.

With starch added the colour change is from blue/black to colourless

The starch should **not** be added until nearly all the iodine has reacted because the blue complex formed with high concentrations of iodine is insoluble and does not re-dissolve as more thiosulfate is added.

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.

Explanation of differing reducing power of halides

A reducing agent donates electrons.

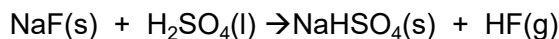
The reducing power of the halides increases down group 7

They have a greater tendency to donate electrons.

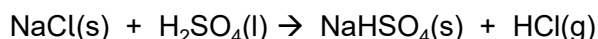
This is because as the ions get bigger it is easier for the outer electrons to be given away as the pull from the nucleus on them becomes smaller.

Fluoride and Chloride

The H_2SO_4 is not strong enough an oxidising reagent to oxidise the chloride and fluoride ions. No redox reactions occur. Only acid-base reactions occur.



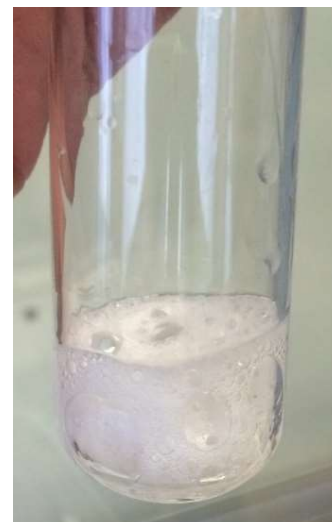
Observations: White steamy fumes of HF are evolved.



Observations: White steamy fumes of HCl are evolved.

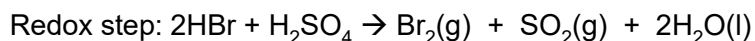
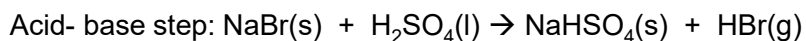
These are acid-base reactions and not redox reactions.

H_2SO_4 plays the role of an acid (proton donor).

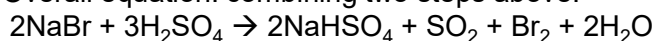


Bromide

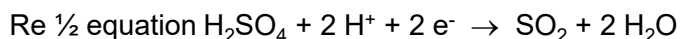
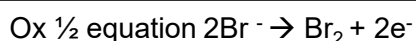
Bromide ions are stronger reducing agents than chloride and fluoride ions. After the initial acid-base reaction the bromide ions reduce the sulfur in H_2SO_4 from +6 to +4 in SO_2



Overall equation: combining two steps above:



Reduction product = sulfur dioxide



Note the sulfuric acid acts as an acid in the first step producing HBr and then acts as an oxidising agent in the second redox step.

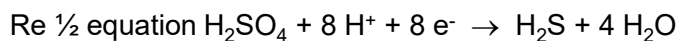
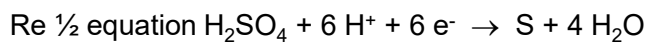
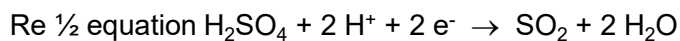
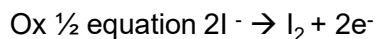
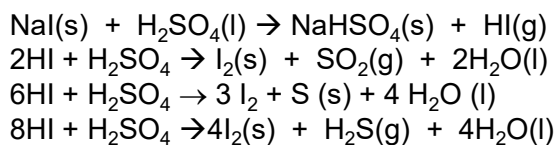
Observations: White steamy fumes of HBr are evolved.

Orange fumes of bromine are also evolved and a colourless, acidic gas SO_2



Iodide

Iodide ions are the strongest halide reducing agents. They can reduce the sulfur from +6 in H_2SO_4 to +4 in SO_2 , to 0 in S and -2 in H_2S .



Reduction products = sulfur dioxide, sulfur and hydrogen sulfide

Note the H_2SO_4 acts as an acid in the first step producing HI and then acts as an oxidising agent in the three redox steps.

Observations:

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

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

A **colourless**, acidic **gas** SO_2

A **yellow solid** of sulfur

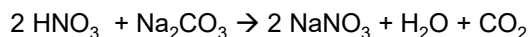
H_2S (hydrogen sulfide), a **gas** with a **bad egg smell**,



The reactions of halide ions with silver nitrate.

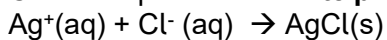
This reaction is used as a test to identify which halide ion is present. The test solution is made acidic with **nitric acid**, and then **silver nitrate solution** is added dropwise.

The role of nitric acid is to react with any carbonate impurities present to prevent formation of the precipitate Ag_2CO_3 . This would mask the desired observations.

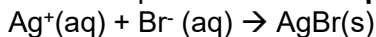


Fluorides produce no precipitate

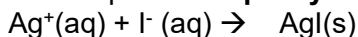
Chlorides produce a **white precipitate**



Bromides produce a **cream precipitate**



Iodides produce a **pale yellow precipitate**



Effect of light on silver halides

The precipitates (except AgI) darken in sunlight forming silver. This reaction is used in photography to form the dark bits on photographic film.

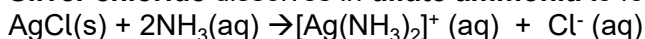
Effect of ammonia on silver halides

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

	AgCl	AgBr	AgI
Addition of aqueous ammonia	Dissolves	Does not dissolve	Does not dissolve
Addition of concentrated ammonia	Dissolves	Dissolves	Does not dissolve

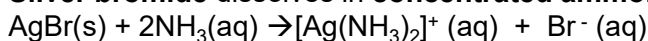
The solubility of the silver halides in ammonia decreases in the order: $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$

Silver chloride dissolves in **dilute ammonia** to form a complex ion



Colourless solution

Silver bromide dissolves in **concentrated ammonia** to form a complex ion

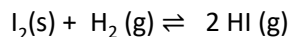
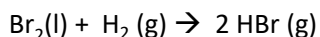
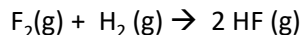


Colourless solution

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

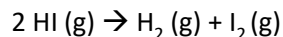
Hydrogen Halides

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.

Thermal stability of halides: Hydrogen iodide will decompose if a hot nichrome wire is plunged into it. Purple vapour of iodine will be seen.

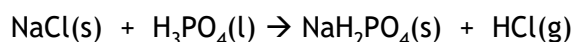


A very hot wire would also decompose hydrogen bromide

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 become bigger their bond length is longer. The bonding pair of electrons gets further from the halogen nuclei.

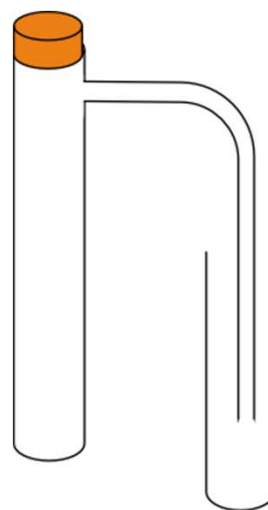
Producing hydrogen halides

Hydrogen halides are made in the laboratory by the reaction of solid sodium halide salts with phosphoric acid.



Observations: White steamy fumes of the hydrogen halides are evolved.

The steamy fumes of HCl are produced when the HCl meets the air because it dissolves in the moisture in the air.



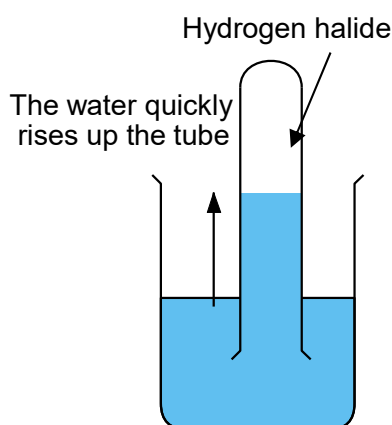
This is the apparatus used to make the hydrogen halide using phosphoric acid.

Notice the downward delivery which is used because the hydrogen halides are more dense than air.

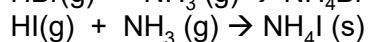
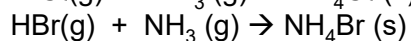
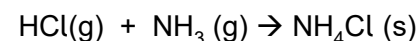
Phosphoric acid is not an oxidising agent and so does not oxidise HBr and HI. Phosphoric acid is more suitable for producing hydrogen halides than the ones with concentrated sulfuric acid to make HCl, HBr, and HI because there are no extra redox reactions taking place and no other products.

Solubility in water :

The hydrogen halides are all soluble in water. They dissolve to form acidic solutions.



All the hydrogen halides react readily with ammonia to give the **white smoke** of the ammonium halide.



This can be used as a test for the presence of hydrogen halides.