

Group 7

Physical Properties

Halogen	Appearance of element at room temperature	Appearance of element in aqueous solution	Appearance of element in hydrocarbon solution
Chlorine	Green gas	Pale green (almost colourless)	Pale green (almost colourless)
Bromine	Red-brown liquid	Orange or yellow	Red
Iodine	Grey-black solid	Brown	Violet

All halogens are diatomic (X_2): as they contain more electrons going down the group, the dispersion forces between the molecules increase, so the **melting and boiling points increase**.

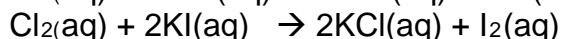
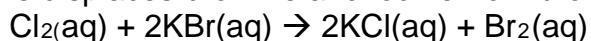
The colour depends on the absorption of light, which in turn depends on an electron jumping to a higher-energy orbital. As the atoms get larger, less energy is needed for an electron to jump into the lowest unoccupied orbital, and so the element absorbs more strongly at longer wavelengths (i.e. in the visible region), and appears darker.

All halogens are soluble in non-polar solvents like hexane. Chlorine is slightly soluble in water, bromine even less, and iodine virtually insoluble.

Tests for Halogens

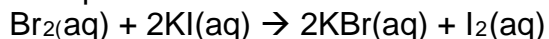
Chlorine turns blue litmus red then bleaches it.

Chlorine displaces bromine and iodine from bromide or iodide solutions.



Bromine is orange/red if dissolved in an organic solvent.

Bromine displaces iodine from an iodide solution.



Iodine turns starch black, is decolourised by thiosulphate solution and is brown in water but purple in organic solvents.

Chemical reactions

The halogens tend to gain electrons to form **halide ions, X⁻**. In the process of gaining an electron, the electron is removed from some other substance, so the halogens tend to be oxidising agents.

Reaction with Metals

The reactivity of the halogens increases up the group. They tend to be reactive with metals, but the vigour of the reaction decreases going down the group. Sodium will burn violently in chlorine;



Sodium will also have vigorous reactions with gaseous bromine and iodine, but the reaction becomes less exothermic as the atomic number of the halogen increases. The heat energy given out in the reaction between sodium and the halogen is shown in the table below.

Halogen	Enthalpy of formation, ΔH_f^θ (NaX) / kJmol^{-1}
Chlorine	-414
Bromine	-361
Iodine	-288

Reaction with non-metals

Halogens also react with non-metals. The reaction with hydrogen illustrates the decreasing reactivity down the group.

Chlorine and hydrogen explode in the presence of sunlight;



Bromine requires heat and the presence of a platinum catalyst to react, while iodine only reacts slowly and the reaction does not go to completion.

Reactions of Halogens as oxidising agents

The reactivity of the halogens increases up the group as they gain electrons more easily. The electron is gained more easily as the empty position it fills is closer to the nucleus and there is less inner shielding electron shielding with the elements high in the group. This means that the elements become stronger oxidising agents going up the group.

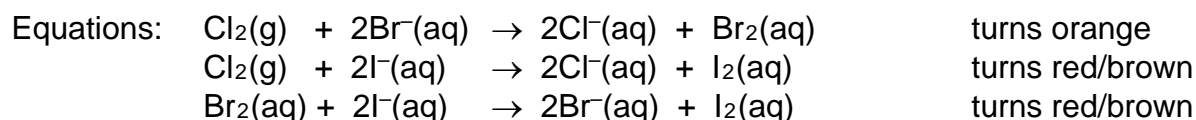
Displacement reactions

The potassium halides indicate the oxidising powers of the Halogens. Halogen displacement reactions using potassium halides illustrate the increasing strength of oxidising power of the halogen going up the group.

Chlorine will oxidise bromide and iodide ions; bromine will oxidise iodide ions; and iodine will not react with either Cl^- or Br^- .

The reactions are illustrated in the table below

Mixture	Appearance of potassium halide solution	Appearance of halogen solution	Appearance after mixing	Conclusion
Potassium iodide + chlorine	Colourless	Colourless	brown	Iodine displaced
Potassium bromide + chlorine	Colourless	Colourless	orange	Bromine displaced
Potassium iodide + bromine	Colourless	orange	brown	Iodine displaced



The salt solutions, e.g. NaCl, NaBr and NaI, are initially colourless.

Oxidation of iron(II)

Iron is a transition metal and it can form compounds of iron(II) and iron(III).

Chlorine is capable of oxidising iron(II) to iron(III).

If chlorine water is added to a pale green solution of containing Fe^{2+} , a yellow solution containing Fe^{3+} is formed.



Bromine is also able to oxidise iron(II) to iron(III), but iodine is not a strong enough oxidising reagent to carry out this reaction.

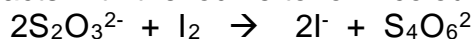
Iodine titrations

Thiosulphate and iodine titrations are used to determine the concentration of oxidising agents.

- First of all the oxidising agent is added to a solution containing excess iodide ions. This oxidises the iodide ions to iodine giving a brown colour.



- Thiosulphate (usually as sodium thiosulphate) is then added from a burette; this reacts with the iodine to form colourless products.



- During the titration, the colour intensity decreases, eventually reaching a pale yellow colour. At this point, a few drops of starch solution are added to give the deep blue complex showing the last traces of iodine.
- Thiosulphate is then added dropwise, until the mixture becomes colourless.
- From a known concentration of thiosulphate, it is possible to determine the number of moles of chemical involved in the reaction.

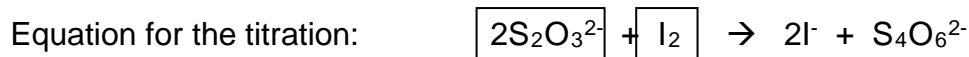
Example

A 0.800g of a contaminated sample of potassium iodate, KIO_3 , was dissolved in 250cm^3 of solution. 25cm^3 of this solution was added to an excess of potassium iodide and dilute sulphuric acid.

The mixture required 21.60cm^3 of 0.1mol dm^{-3} sodium thiosulphate solution to remove the iodine released.

Calculate the percentage purity of the potassium iodate.

Moles of sodium thiosulphate = $21.60 / 1000 \times 0.1 = 0.00216 \text{ mol}$



Moles of iodine = $0.00216 / 2 = 0.00108 \text{ mol}$



Moles of iodate in the 25cm^3 sample = $0.00108 / 3 = 0.00036 \text{ mol}$

Moles of iodate in the 250cm^3 solution = $0.00036 \times 250 / 25 = 0.0036$

Mass of pure potassium iodate = $0.0036 \times 214 = 0.7704\text{g}$

Percentage purity = $0.7704 / 0.8000 \times 100 = 96.3\%$

Reactions with Concentrated Sulphuric Acid

When concentrated sulphuric acid is added to a potassium halide, hydrogen halide is formed. **With a chloride misty white fumes appear.**



The chloride ion is not a strong enough reducing agent to have a further reaction.

Concentrated sulphuric acid is an oxidising agent and reacts further with the bromide and iodide.

Bromide ions reduce the sulphuric acid to sulphur dioxide. **Orange-brown misty fumes appear.**

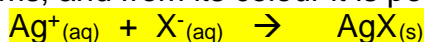


Iodide ions can produce a variety of reactions forming sulphur dioxide, sulphur and hydrogen sulphide.



Identification of halide ions

To test a substance to see if it contains chloride, bromide or iodide ions, the substance is dissolved in water, acidified with dilute nitric acid, and then silver nitrate solution is added. A precipitate of silver halide forms, and from its colour it is possible to identify the halide.



The effect of sunlight on the precipitate or addition of ammonia solution to the precipitate can then be used to confirm the result.

Halide	Silver nitrate	Effect of sunlight	Ammonia solution
Chloride	White precipitate	White precipitate turns purple-grey	Precipitate dissolves.
Bromide	Cream precipitate	Cream precipitate turns green-yellow	In dilute ammonia, precipitate partially dissolves. In concentrated ammonia precipitate dissolves.
Iodide	Yellow precipitate	No effect	Precipitate does not dissolve.

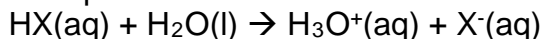
Reactions of hydrogen halides

In water

The hydrogen halides are soluble in water, and when dissolved in they split up (dissociate) into ions forming an acidic solution.



HCl is strongly acidic due to complete dissociation.



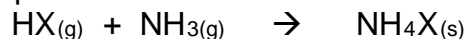
Hydrogen ions H^+ or hydroxonium ions, H_3O^+ , provide the acidity.

The relative acid strength is $\text{HF} \ll \text{HCl} < \text{HBr} < \text{HI}$.

HI is the strongest acid as it has the weakest bond (H-I). It is therefore more easily dissociated into H^+ or H_3O^+ ions.

With ammonia

When gaseous hydrogen halides come into contact with gaseous ammonia, dense white smoke of ammonium halide is produced.



The +1 and +5 oxidation states of chlorine

All the halogens except for fluorine exhibit a number of positive oxidation states. These are due to the promotion of electrons from p orbitals into vacant d orbitals.

Chloric (I) acid HClO forms salts called chlorate(I)'s e.g. NaClO. which contain the ion ClO⁻.

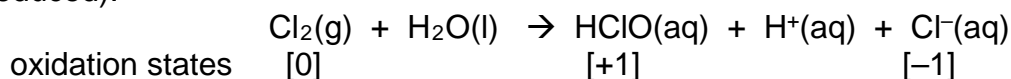
Chloric acid (V) HClO₃ forms a series of salts called chlorate(V)'s.

For example NaClO₃ contains the ion ClO₃⁻.

These salts and acids are all good oxidising agents.

Chlorine as a bleach

Chlorine is sparingly soluble in water. Some of the dissolved chlorine reacts in a **disproportionation** reaction (one in which an element is simultaneously oxidised and reduced):



HClO, or chloric(I) acid, is called a bleach, since it is able to oxidise coloured compounds such as litmus. It will also kill bacteria by oxidising them.

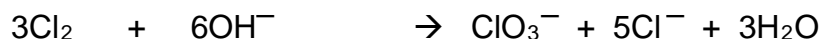
This is made use of in water purification. The water supply is treated with sufficient chlorine to give a concentration of about 0.5 mg dm⁻³. At this level, harmful organisms are killed, but humans can drink the water without effect (other than a slight odour).

Chlorine and alkali

When chlorine is passed into cold dilute sodium hydroxide solution, it disproportionates to chlorate(I) and chloride:



If, instead, chlorine is passed into a hot, concentrated solution of sodium hydroxide, the disproportionation goes further, forming chlorate(V) and chloride – note that one Cl goes up by 5 oxidation numbers (0 to +5), and five Cls go down by one (0 to -1):



The chlorate(V) can be extracted by filtration and purified by recrystallisation as it is less soluble in water than the chloride.

Similar reactions occur for bromine and iodine: these go all the way to BrO₃⁻ and IO₃⁻ even in dilute solution.