4B Halogens

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

Trend 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

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

1. 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

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**

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

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

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

The oxidation reactions of metals and metal ion by halogens.

$Br_2(l) + 2Na(s) \rightarrow 2NaBr(s)$

$2Na \rightarrow 2Na^+ + 2e^-$

$Br_2 + 2e^- \rightarrow 2Br^-$

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

$3Cl_2(g) + 2Fe(s) \rightarrow 2FeCl_3(s)$

$Br_2(l) + Mg(s) \rightarrow MgBr_2(s)$

$Cl_2(g) + 2Fe^{2+}(aq) \rightarrow 2Cl^-(aq) + 2Fe^{3+}(aq)$

$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$

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

The disproportionation reactions of chlorine and chlorate(I).

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

Chlorine is both simultaneously reducing and oxidising changing its oxidation number from 0 to -1 and 0 to +1

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

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.

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

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.

Reaction of halogens with cold dilute NaOH solution:

Cl_2, Br_2, and I_2 in aqueous solutions will react with cold sodium hydroxide. 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 is used as Bleach and to disinfect/ 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.

$3Cl_2(aq) + 6NaOH(aq) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$

$3I_2(aq) + 6NaOH(aq) \rightarrow 5NaI(aq) + NaIO_3(aq) + 3H_2O(l)$

$3I_2(aq) + 6OH^-(aq) \rightarrow 5I^-(aq) + IO_3^-(aq) + 3H_2O(l)$

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)
$NaClO_3$: sodium chlorate(V)
K_2SO_4 potassium sulfate(VI)
K_2SO_3 potassium sulfate(IV)

The reaction of halide salts with concentrated sulphuric 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 sulphuric 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

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.

$NaF(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HF(g)$

Observations: White steamy fumes of HF are evolved.

$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$

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

Br- ions are stronger reducing agents than Cl- and F- and after the initial acid-base reaction reduce the Sulphur in H_2SO_4 from +6 to + 4 in SO_2

Acid- base step: $NaBr(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HBr(g)$

Redox step: $2HBr + H_2SO_4 \rightarrow Br_2(g) + SO_2(g) + 2H_2O(l)$

Observations: White steamy fumes of HBr are evolved.

Red fumes of Bromine are also evolved and a colourless, acidic gas **SO_2**

Ox ½ equation $2Br^- \rightarrow Br_2 + 2e^-$

Re ½ equation $H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

Reduction product = sulphur dioxide

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

$NaI(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HI(g)$
$2HI + H_2SO_4 \rightarrow I_2(s) + SO_2(g) + 2H_2O(l)$
$6HI + H_2SO_4 \rightarrow 3I_2 + S(s) + 4H_2O(l)$
$8HI + H_2SO_4 \rightarrow 4I_2(s) + H_2S(g) + 4H_2O(l)$

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 Sulphur
H_2S (Hydrogen Sulphide), a **gas** with a **bad egg smell**,

Ox ½ equation $2I^- \rightarrow I_2 + 2e^-$

Re ½ equation $H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

Re ½ equation $H_2SO_4 + 6H^+ + 6e^- \rightarrow S + 4H_2O$

Re ½ equation $H_2SO_4 + 8H^+ + 8e^- \rightarrow H_2S + 4H_2O$

Reduction products = sulphur dioxide, sulphur and hydrogen sulphide

Note the H_2SO_4 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

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 carbonates present to prevent formation of the precipitate Ag_2CO_3. This would mask the desired observations

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

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

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:

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.

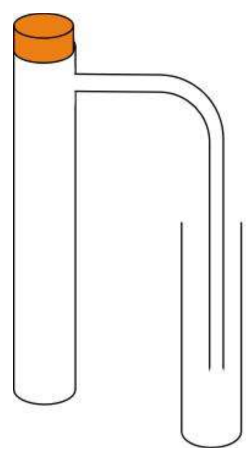
Producing hydrogen halides

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

$NaCl(s) + H_3PO_4(l) \rightarrow NaH_2PO_4(s) + HCl(g)$

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



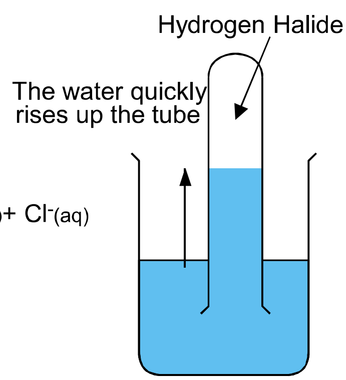
This is the apparatus used to make the hydrogen halide using phosphoric acid.

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 sulphuric 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.

$HCl_{(g)} + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$



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

$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
$HBr(g) + NH_3(g) \rightarrow NH_4Br(s)$
$HI(g) + NH_3(g) \rightarrow NH_4I(s)$

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

4C Analysis of Inorganic Compounds

Testing for Negative ions (anions)

Testing for Presence of a carbonate CO_3^{2-} and hydrogencarbonates HCO_3^-

Add any dilute acid and observe effervescence.
Bubble gas through limewater to test for CO_2 – will turn limewater cloudy

$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$

$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$

$HCl + NaHCO_3 \rightarrow NaCl + H_2O + CO_2$

$H^+ + HCO_3^- \rightarrow H_2O + CO_2$

Fizzing due to CO_2 would be observed if a carbonate or a hydrogencarbonate was present

Testing for Presence of a sulfate

Acidified $BaCl_2$ solution is used as a reagent to test for sulfate ions

If **Barium Chloride** is added to a solution that contains sulfate ions a **white precipitate** forms

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$.

Other anions should give a negative result which is no precipitate forming

The acid is needed to react with carbonate impurities that are often found in salts which would form a white Barium carbonate precipitate and so give a false result

Sulfuric acid cannot be used to acidify the mixture because it contains sulfate ions which would form a precipitate

Testing for 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.

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$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
Iodides produce a **pale yellow** precipitate
$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

Hydrochloric acid cannot be used to acidify the mixture because it contains chloride ions which would form a precipitate

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

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

Testing for positive ions (cations)

Test for ammonium ion NH_4^+, by reaction with warm NaOH(aq) forming NH_3

$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

Ammonia gas can be identified by its pungent smell or by turning red litmus paper blue

See flame tests on page 4 for more cation tests