2.3 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.

**Trend in melting point and boiling point**

Increase down the group
As the molecules become larger they have more electrons and so have larger van der waals 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.

1. The displacement 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.

Fluorides produce no precipitate
Chlorides produce a white precipitate
Ag⁺(aq) + Cl⁻ (aq) → AgCl(s)
Bromides produce a cream precipitate
Ag⁺(aq) + Br⁻ (aq) → AgBr(s)
Iodides produce a pale yellow precipitate
Ag⁺(aq) + I⁻ (aq) → AgI(s)

Chlorine will displace both bromide and iodide ions; bromine will displace iodide ions know these observations!

<table>
<thead>
<tr>
<th>Chlorine (aq)</th>
<th>Bromine (aq)</th>
<th>Iodine (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium chloride (aq)</td>
<td>Very pale green solution, no reaction</td>
<td>Yellow solution, no reaction</td>
</tr>
<tr>
<td>Potassium bromide (aq)</td>
<td>Yellow solution, Cl has displaced Br</td>
<td>Yellow solution, no reaction</td>
</tr>
<tr>
<td>Potassium iodide (aq)</td>
<td>Brown solution, Cl has displaced I</td>
<td>Brown Solution, Br has displaced I</td>
</tr>
</tbody>
</table>

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)

Be able to write these reactions as two half equations showing oxidation or reduction e.g. 2Br⁻ (aq)→Br₂ (aq)+ 2e⁻
Cl₂ (aq)+ 2e⁻→ 2Cl⁻ (aq)

2. 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.

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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) + 2NH₃(aq) →[Ag(NH₃)₂]⁺ (aq) + Cl⁻ (aq)
Colourless solution

**Silver bromide** dissolves in concentrated ammonia to form a complex ion
AgBr(s) + 2NH₃(aq) →[Ag(NH₃)₂]⁺ (aq) + Br⁻ (aq)
Colourless solution

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

2 HNO₃ + Na₂CO₃ → 2 NaNO₃ + H₂O + CO₂
3. 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.

**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

F⁻ and Cl⁻ ions are not strong enough reducing agents to reduce the S in H₂SO₄.

No redox reactions occur. Only acid-base reactions occur.

\[
\text{NaF(s) + H}_2\text{SO}_4(l) \rightarrow \text{NaHSO}_4(s) + \text{HF(g)}
\]

Observations: White steamy fumes of HF are evolved.

\[
\text{NaCl(s) + H}_2\text{SO}_4(l) \rightarrow \text{NaHSO}_4(s) + \text{HCl(g)}
\]

Observations: White steamy fumes of HCl are evolved.

These are acid–base reactions and not redox reactions. H₂SO₄ 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 sulfur in H₂SO₄ from +6 to + 4 in SO₂.

Acid-base step: NaBr(s) + H₂SO₄(l) → NaHSO₄(s) + HBr(g)

Redox step: 2HBr + H₂SO₄ → Br₂(g) + SO₂(g) + 2H₂O(l)

Observations: White steamy fumes of HBr are evolved.

Note the H₂SO₄ plays the role of acid in the first step producing HBr and then acts as an oxidising agent in the second redox step.

**Ox ½ equation** 2Br⁻ → Br₂ + 2e⁻

**Re ½ equation** H₂SO₄ + 2 H⁺ + 2 e⁻ → SO₂ + 2 H₂O

### Iodide

I⁻ ions are the strongest halide reducing agents. They can reduce the sulfur from +6 in H₂SO₄ to + 4 in SO₂, to 0 in S and -2 in H₂S.

\[
\text{NaI(s) + H}_2\text{SO}_4(l) \rightarrow \text{NaHSO}_4(s) + \text{HI(g)}
\]

\[
\begin{align*}
2 \text{HI} & + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2(s) + \text{SO}_2(g) + 2 \text{H}_2\text{O(l)} \\
6 \text{HI} & + \text{H}_2\text{SO}_4 \rightarrow 3 \text{I}_2 + \text{S} + 4 \text{H}_2\text{O (l)} \\
8 \text{HI} & + \text{H}_2\text{SO}_4 \rightarrow 4 \text{I}_2(s) + \text{H}_2\text{S(g)} + 4 \text{H}_2\text{O(l)}
\end{align*}
\]

Observations:

- **White steamy fumes of HI are evolved.**
- **Black solid and purple fumes of Iodine are also evolved.**
- **A colourless, acidic gas SO₂**
- **A yellow solid of sulfur H₂S (Hydrogen sulfide), a gas with a bad egg smell,**

Reduction products = sulfur dioxide, sulfur and hydrogen sulfide

Note the H₂SO₄ 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**
4. The disproportionation reactions of chlorine.

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

**Chlorine with water:**

\[
\text{Cl}_2 (g) + \text{H}_2\text{O} (l) \rightleftharpoons \text{HClO} (aq) + \text{HCl} (aq)
\]

Chlorine is both simultaneously reducing and oxidising.

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.

**Reaction with water in sunlight**

If the chlorine is bubbled through water in the presence of bright sunlight a different reaction occurs.

\[
2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{Cl}^- + \text{O}_2
\]

The same reaction occurs to an equilibrium mixture of chlorine water when standing in sunlight. The greenish colour of chlorine water fades as the Cl\(_2\) reacts and a colourless gas (O\(_2\)) is produced.

The 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 chlorine with cold dilute NaOH solution:**

Cl\(_2\), (and Br\(_2\), I\(_2\)) in aqueous solutions will react with cold sodium hydroxide. The colour of the halogen solution will fade to colourless.

\[
\text{Cl}_2 (aq) + 2 \text{NaOH} (aq) \rightarrow \text{NaCl} (aq) + \text{NaClO} (aq) + \text{H}_2\text{O} (l)
\]

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

**Naming chlorates/sulfates**

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\(_2\)SO\(_4\): potassium sulfate(VI)
K\(_2\)SO\(_3\): potassium sulfate(IV)