Chapter 12 (AS-Level)

Group VII

These are called the halogens. They are non-metals.

General properties of group VII elements

- They behave in a similar chemical manner
- Non-metals
- Exist as diatomic molecules
- Melting and boiling points increase down the group
- Colour deepens down the group
- Very reactive and readily form salts
- Can exist in covalent and ionic compounds
- Reactivity decreases down the group
- They exhibit a range of oxidation numbers
- Electronegativity decrease down the group
- Their oxidation power decrease as going down the group

The reactivity of halogens

Displacement reactions

- The electron affinity (enthalpy change for $X + e^- \rightarrow X^-$) is the ease at which a halogen can become an ion. The more negative the greater this ease and the greater the power of the oxidizing of the halogen
- The oxidizing power of the halogens decrease down the group as their reaction affinity increases (nearer to positive)
- Displacement reactions can occur as the oxidizing power of the halogens decrease down the group and any halogen can displace any other halogen lower in the group

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

  Cyclohexane is used, which forms a separate layer in which the ions are more soluble in it, so the colour becomes more apparent.

Halogen	Cl^-	Br^-	I^-
Cl_2	-	Orange-yellow	Purple iodine
Br_2	No reaction	-	Purple iodine
I_2	No reaction	No reaction	-

Reactions of halides with H_2

- $H_2 + X_2 \rightarrow 2\ HX$

  $H_2 + Cl_2 \rightarrow 2\ HCl$ (explosive in UV light)

  $H_2 + Br_2 \rightarrow 2\ HBr$ (reaction slow on heating)

  $H_2 + I_2 \rightarrow 2\ HI$ (incomplete reaction on heating)

- All hydrogen halides formed are simple molecular compounds which are gases at room temperature
- The H-X bond length increases down the group, so the bond enthalpy decreases
- The bond enthalpy decreases down the group. This means that the stability of the hydrogen halides also decrease down the group
  HCl is stable at 1500°C
  HBr decomposes at 800°C
  HI decomposes ate 500°C. This is the least stable and can act as a strong reducing agent.

Test for halides

(1) Acidify with nitric acid
(2) Add aq. Silver nitrate
White precipitate (silver chloride) → Chloride ion
Cream precipitate (silver bromide) → Bromide ion
Yellow precipitate (silver iodide) → Iodide ion
(3) Add NH_3 (aq)
White precipitate (silver chloride) dissolves in dilute → colourless solution
Cream precipitate (silver bromide) dissolves in excess → colourless solution
Yellow precipitate (silver iodide) doesn't dissolve

Another test is with concentrated H_2SO_4:

(1) With Cl^-
$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ (white fumes)
(2) With Br^- and I^-
H_2SO_4 is an oxidizing agent and oxidize HBr and HI into Br_2 and I_2, and their colours can be seen.
With HBr, sulphuric acid is reduced by HBr into SO_2

$$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$$
$$2\ HBr + H_2SO_4 \rightarrow H_2O + Br_2 + SO_2 \text{ } (Br_2 \text{ is an orange vapour})$$

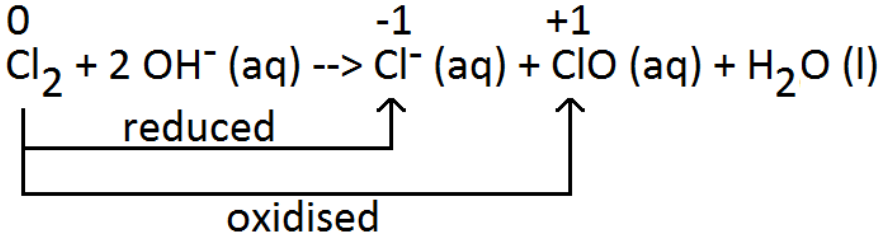
With NaI, sulphuric acid is reduced by HI into SO_2, S and H_2S

$$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$$
$$2\ HI + H_2SO_4 \rightarrow 2\ H_2O + I_2 + SO_2$$
$$6\ HI + H_2SO_4 \rightarrow 4\ H_2O + 3\ I_2 + S$$
$$8\ Hi + H_2SO_4 \rightarrow 4\ H_2O + 4\ I_2 + H_2S$$

Disproportionation reactions of chlorine

This happens in the reactions of chlorine with sodium hydroxide. These depend on the temperature:

- With cold dilute aq. NaOH, a mix of Cl^- and ClO^- (chlorate ions) is formed.
$$Cl_2 + 2\ NaOH\ (aq) \rightarrow NaCl\ (aq) + NaClO\ (aq) + H_2O$$
This is disproportionation, in which chlorine is oxidized and reduced at the same time.



This reaction is used to produce bleach which is HClO, chloric acid. It is a solution of NaCl and NaClO in a 1:1 mole ratio.

- With hot concentrated aq. NaOH, forms Cl- and Chlorate (v) (ClO3-) ions:

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

Purification of drinking water

When Cl2 gas is used to purify drinking water, disproportionation occurs again to make HCl and HClO.

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

The HClO (chloric acid) decomposes into HCl and O which kill the bacteria.

Uses of halogens

- Cl2 and Cl2 (aq) are used as oxidizing agents, bleaches, treating drinking water and treating swimming pool water. Also used in the manufacture of various chemicals like chloroethene and CFCs which are used as fire extinguishers and are vital constituent of artificial blood. Solvents that contain chlorine such as di-chloromethane are used to dissolve fats and oils.

- Fluorine is used to make CFCs, PTFE (polytetrafluoroethene) which is used as a lubricant, a coating for non-stick pans, electrical insulation and in water proof clothing. Fluoride ions are used to prevent tooth decay. Hydrofluoric acid is used in etching glass. Bromochlorodifluoromethane is sued in fire extinguishers.

- Silver bromide is used in photographic film.

- Iodine is an essential part of our diet, and an imbalance causes thyroid problems. A solution of iodine is sometimes used as an antiseptic.

END OF LESSON