Group 7, the halogens

Physical trends, displacement and redox reactions, disproportionation of chlorine, reactions of halide salts with sulfuric acid, silver nitrate tests, and predictions about fluorine and astatine.

Physical properties

Halogen	State at room temperature	Colour of element	In water	In hexane (non-polar solvent)
Chlorine, Cl_2	Gas	Pale yellow-green	Very pale green	Pale green
Bromine, Br_2	Liquid	Red-brown	Orange	Orange-red
Iodine, I_2	Solid	Grey-black (purple vapour)	Brown	Violet

Trends down the group

- **Melting and boiling temperatures increase.** The molecules are diatomic and held by London forces, which are stronger as the number of electrons increases.
- **Electronegativity decreases.** The atoms get bigger and the outer shell is further from the nucleus, more shielded, so the attraction for a bonding pair weakens.
- **Reactivity decreases.** Each halogen atom must gain one electron to form a halide ion. Down the group the incoming electron is further from the nucleus and more shielded, so it is attracted less strongly. Fluorine is the most reactive.

Displacement reactions

A more reactive halogen oxidises the halide ions of a less reactive one. This shows the trend in oxidising power: $Cl_2 > Br_2 > I_2$.

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

Halogen added to	Cl^-	Br^-	I^-
Chlorine water	No reaction	Orange (bromine)	Brown (iodine)
Bromine water	No reaction	No reaction	Brown (iodine)

Note Academy

Adding hexane and shaking makes the colours clearer: bromine is orange-red and iodine violet in the upper layer.

> **NOTE**
>
> In each case the halogen is reduced (its oxidation number falls from 0 to −1) and the halide ion is oxidised (−1 to 0).

Reactions of halogens with metals

Halogens oxidise metals: $2Na + Cl_2 \rightarrow 2NaCl$ and $Mg + Br_2 \rightarrow MgBr_2$. The halogen goes from 0 to −1.

Disproportionation of chlorine

Chlorine is simultaneously oxidised and reduced in these reactions.

- **With water:** $Cl_2 + H_2O \rightleftharpoons HClO + HCl$. Chlorine goes from 0 to +1 (in chloric(I) acid) and −1. Chloric(I) acid kills bacteria, so chlorine is used in **water treatment**. (The reaction is reversible, and chlorine is a hazard because it is toxic.)
- **With cold, dilute sodium hydroxide:** $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$. Sodium chlorate(I), $NaClO$, is **bleach**.
- **With hot, concentrated alkali:** $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$. Chlorine goes from 0 to −1 and +5 (sodium chlorate(V)).

Bromine and iodine behave in the same way as chlorine.

Halides with concentrated sulfuric acid

Solid sodium (or potassium) halides react with concentrated sulfuric acid. The products show the increasing **reducing power** of the halide ions down the group: $I^- > Br^- > Cl^-$.

Halide	Observations	Products	Role of halide
Chloride	Steamy white fumes of HCl	$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$	Not a reducing agent; acid-base only
Bromide	Steamy fumes, then orange-brown vapour (Br_2) and a choking gas (SO_2)	HBr, Br_2, SO_2, H_2O	Reduces H_2SO_4 from +6 to +4
Iodide	Purple vapour (I_2), yellow solid (S), smell of rotten eggs (H_2S), black solid	I_2, S, H_2S	Reduces H_2SO_4 from +6 to +4, 0 and −2

Note Academy

The hydrogen halides get progressively easier to oxidise down the group, because the larger iodide ion loses an electron more easily than the bromide or chloride. This is why HI can reduce sulfuric acid all the way to H_2S, but HCl cannot reduce it at all.

Tests for halide ions

Add dilute nitric acid (to remove carbonate), then aqueous silver nitrate.

Halide	Precipitate	Dissolves in
Chloride	White ($AgCl$)	Dilute aqueous ammonia
Bromide	Cream ($AgBr$)	Concentrated aqueous ammonia only
Iodide	Yellow (AgI)	Insoluble in ammonia

$$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$$

Hydrogen halides

- With **ammonia** gas they make white smoke of ammonium halide: $NH_3 + HCl \rightarrow NH_4Cl$.
- With **water** they dissolve to give strongly acidic solutions: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$.

Predictions

Using the trends, predict that **fluorine** is a very pale yellow gas, the most reactive and most electronegative halogen, and that it displaces all other halides. Predict that **astatine** is a black solid with the lowest reactivity, that At^- is a very strong reducing agent, and that silver astatide is yellow-white and insoluble in ammonia.

Note Academy