Group 17

A-Level Chemistry

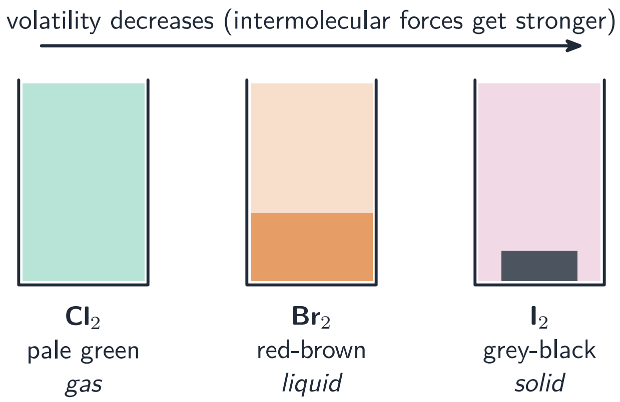
Physical properties of the halogens

Bromine is a Group 17 halogen —a dark liquid that gives off an orange vapour.

The **halogens** 卤素 are the **Group** 族 17 elements. They exist as diatomic molecules (Cl_2, Br_2, I_2). Going down the group:

Element	Colour and state at room temperature
chlorine	pale green gas
bromine	red-brown liquid
iodine	grey-black solid (purple vapour)

The **volatility** 挥发性 (how easily a substance turns to vapour) **decreases** down the group: chlorine is a gas, but iodine is a solid. This is because the molecules get larger and have more electrons, so the **instantaneous dipole** 瞬时偶极 and **induced dipole** 诱导偶极 forces between them get stronger. Stronger forces are harder to break, so the boiling point rises and volatility falls.



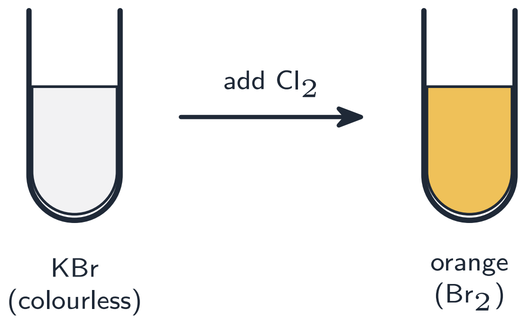
Down Group 17 the halogens change from a pale green gas to a red-brown liquid to a grey-black solid as volatility falls

The **bond energy** 键能 (bond strength) of the X–X molecules generally falls from Cl_2 to I_2, because the shared electrons are further from the nuclei in the larger atoms.

Chemical properties of the halogens and hydrogen halides

Halogens as oxidising agents

Each halogen reacts by gaining one electron to form a 1− ion, so it acts as an **oxidising agent** 氧化剂. This power **decreases** down the group, because the larger atoms attract an extra electron less strongly. A more reactive halogen can push out a less reactive one from its salt:



Chlorine displaces bromine: the solution turns orange

$$Cl_2 + 2KBr \rightarrow 2KCl + Br_2$$

Reactions with hydrogen

Each halogen reacts with hydrogen to form a **hydrogen halide** 卤化氢:

$$H_2 + Cl_2 \rightarrow 2HCl$$

The reaction gets less vigorous down the group: chlorine reacts explosively in light, bromine needs heat, and iodine reacts slowly and only partly.

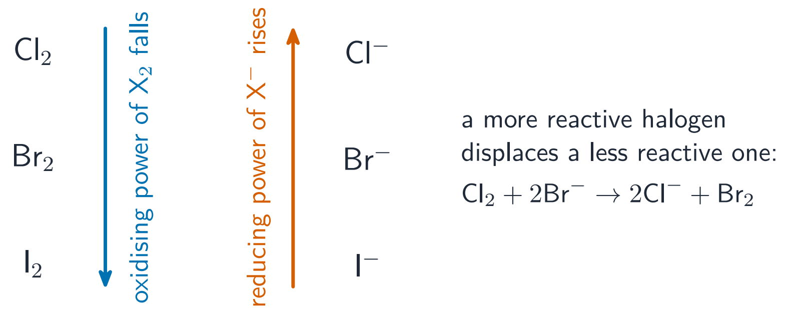
Thermal stability of the hydrogen halides

The **thermal stability** 热稳定性 of the hydrogen halides **decreases** down the group. The H–X bond gets weaker as the halogen atom gets larger, so HI breaks apart on gentle heating while HCl is very stable.

Reactions of the halide ions

Halide ions as reducing agents

A **halide ion** 卤离子 (such as Cl^-) can give away an electron, acting as a **reducing agent** 还原剂. This power **increases** down the group, because a larger ion holds its outer electron less tightly.

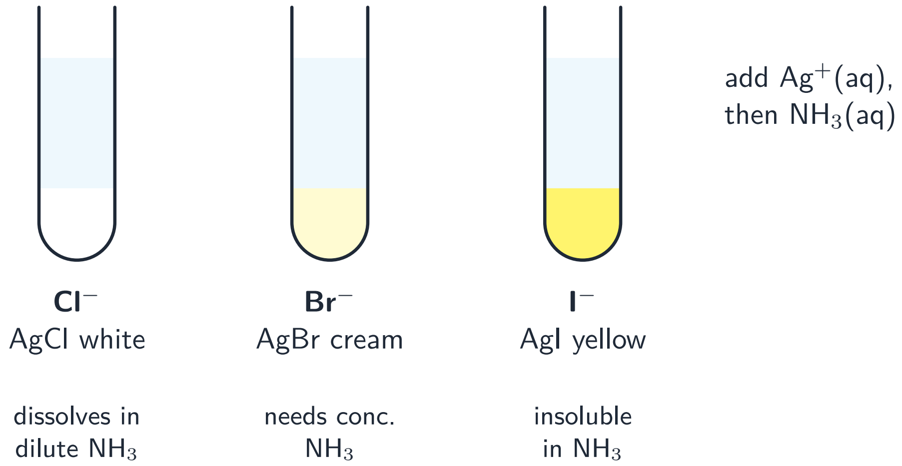


Two opposite trends: the oxidising power of the halogens falls down the group, while the reducing power of the halide ions rises

Reaction with aqueous silver ions

Add aqueous silver nitrate, then aqueous **ammonia** 氨, to identify the halide from the colour of the silver halide **precipitate** 沉淀:

Halide	**Precipitate with Ag^+**	**Solubility in ammonia**
Cl^-	white	dissolves in dilute ammonia
Br^-	cream	dissolves only in concentrated ammonia
I^-	yellow	insoluble in ammonia



Silver halide precipitates: AgCl is white, AgBr cream and AgI yellow —and their solubility in ammonia confirms which halide is present

The silver halide test: AgCl is white, AgBr cream and AgI yellow

Reaction with concentrated sulfuric acid

All the halides first give the hydrogen halide. The lower halides are then oxidised by the acid, because they are stronger reducing agents:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

- chloride gives only HCl (no redox).
- bromide also gives some brown Br_2 and SO_2.
- iodide gives I_2 and the smelly gases H_2S and SO_2, because I^- is the strongest reducing agent.

reducing power increases

$Cl^- \rightarrow$ HCl only (no redox)

$Br^- \rightarrow$ HBr, then $Br_2 + SO_2$

$I^- \rightarrow$ HI, then $I_2 + H_2S + SO_2$

With concentrated sulfuric acid, chloride gives only HCl, but bromide and iodide (stronger reducing agents) are also oxidised to the halogen

Reactions of chlorine

Chlorine is added to pool water to kill microbes.

With sodium hydroxide

With **cold, dilute** sodium hydroxide, chlorine reacts to form chloride and chlorate(I):

$$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$$

With **hot, concentrated** sodium hydroxide, it forms chloride and chlorate(V):

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

In both, the **oxidation number 氧化数** of chlorine goes both up and down (from 0), so both are **disproportionation 歧化** reactions.

Chlorine in water purification

A little chlorine is added to water for **water purification** 水净化. It reacts with water:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

The active species HOCl and ClO^- kill **bacteria** 细菌, making the water safe to drink.

Worked example. Solid NaCl, NaBr and NaI are each warmed with concentrated H_2SO_4. Predict the products. **Reducing power increases down the group**, so how far each halide reduces the sulfuric acid differs. Cl^- is too weak to reduce it at all, so you get only steamy HCl - an acid-base reaction. Br^- reduces it a little: HBr plus brown Br_2 and SO_2. I^- is the strongest reducing agent: HI plus I_2, and it drives the sulfur all the way down to H_2S, with its bad-egg smell. **Every** halide gives the hydrogen halide first; the extra products appear only where the halide is a strong enough **reducing agent** to attack the sulfur.

Exam tips

- Halogens get **less reactive down** the group (harder to gain an electron); oxidising power decreases.
- **Displacement**: a more reactive halogen displaces a less reactive halide —state the colour change.
- Test halide ions with $AgNO_3$: white (Cl^-), cream (Br^-), yellow (I^-), then confirm with dilute/concentrated ammonia.
- Chlorine with water and with cold NaOH are **disproportionation** —show the oxidation-number changes.