

Group 17

A-Level Chemistry 9701 · Topic 11 revision notes

Everything from the 4 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Physical properties of the halogens

3. Reactions of the halide ions

2. Halogens as oxidising agents and the hydrogen halides

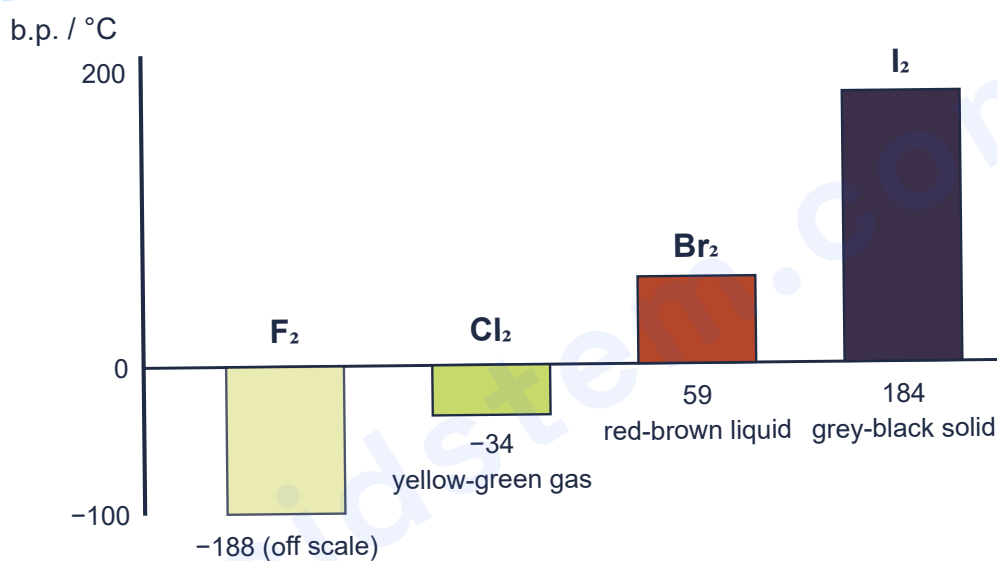
4. Chlorine: disproportionation and water treatment

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1 Physical properties of the halogens

Syllabus 11.1

The halogens exist as diatomic molecules, X_2 . Down the group the molecules have **more electrons**, so the **instantaneous dipole-induced dipole forces** between them get stronger and the boiling points rise: **volatility decreases** from chlorine (a gas) to bromine (a liquid) to iodine (a solid). The colours deepen too. Within each molecule, the X-X **bond energy decreases** from Cl-Cl to I-I as the atoms get larger and the bonding pair is further from the nuclei; F-F is anomalously weak because the small atoms' lone pairs repel each other.



more electrons down the group: stronger id-id forces, less volatile

Fig. 1: boiling points and appearance of the halogens

Forces between molecules versus the bond inside.

- ✓ **Cl₂** gas, **Br₂** liquid, **I₂** solid.
- ✓ **Volatility** falls: more electrons, stronger id-id.
- ✓ **Bond energy** falls Cl-Cl > Br-Br > I-I.
- ✓ **F-F** anomalously weak: lone-pair repulsion.

Watch out!

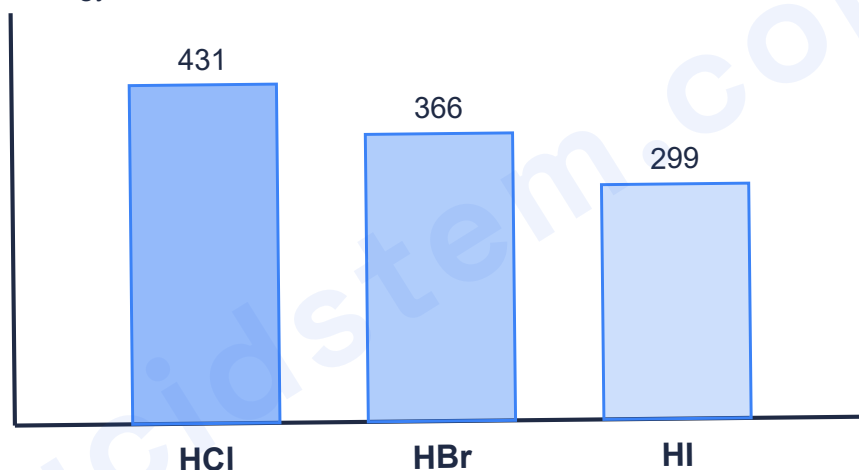
Boiling a halogen breaks **intermolecular** forces, not the X-X covalent bond. The rise in boiling point and the fall in bond energy are separate trends with separate explanations: one is about forces between molecules, the other about the bond inside each molecule.

2 Halogens as oxidising agents and the hydrogen halides

Syllabus 11.2

Halogens are **oxidising agents**: they gain electrons to form halide ions. **Oxidising power decreases down the group** ($\text{Cl}_2 > \text{Br}_2 > \text{I}_2$) because larger atoms attract an incoming electron less strongly. So a halogen **displaces** any halogen below it from a solution of its halide. The halogens react with hydrogen less and less vigorously down the group, and the **thermal stability of the hydrogen halides decreases** from HCl to HI because the H-X bond gets longer and weaker.

H-X bond energy / kJ mol^{-1}



longer, weaker H-X bond: HI decomposes most easily on heating

Fig. 1: H-X bond energies fall down the group

Higher halogen displaces lower halide.

- ✓ **Oxidising power:** $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$.
- ✓ **Colours in hexane:** Br_2 orange-red, I_2 purple.
- ✓ **H-X bond energy** falls, so HX stability falls.
- ✓ **Halogen** reduced; **halide** oxidised.

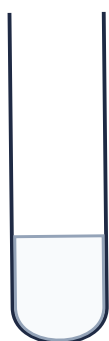
Watch out!

Oxidising power **decreases** down the group, so iodine cannot oxidise chloride or bromide ions. When explaining displacement, identify the halogen as the oxidising agent and the halide ion as the reducing agent. For thermal stability, refer to the **H-X bond energy**, not to intermolecular forces.

3 Reactions of the halide ions

Syllabus 11.3

Halide ions act as **reducing agents**, losing electrons to form halogens. **Reducing power increases down the group** ($I^- > Br^- > Cl^-$) because the outer electrons of a larger ion are further from the nucleus and more easily lost. With concentrated sulfuric acid, chloride gives only HCl; bromide also reduces the acid to SO_2 (S: +6 $\rightarrow$ +4); iodide reduces it as far as S and H_2S (S: +6 $\rightarrow$ -2). To **test** for halides, acidify with dilute nitric acid and add $AgNO_3(aq)$: AgCl is white, AgBr cream, AgI yellow, distinguished further by their solubility in ammonia.



AgCl
white

dissolves in dilute NH_3



AgBr
cream

dissolves in conc. NH_3



AgI
yellow

insoluble in NH_3

add dilute HNO_3 then $AgNO_3(aq)$, then test the precipitate with ammonia

Fig. 1: the silver halide precipitates and their solubility in aqueous ammonia

Bigger ion, stronger reducing agent.

- ✓ **Reducing power:** $I^- > Br^- > Cl^-$.
- ✓ **Conc. H_2SO_4 :** Cl^- HCl only; Br^- to SO_2 ; I^- to H_2S .
- ✓ **$AgNO_3$:** white, cream, yellow.
- ✓ **Ammonia:** dilute dissolves $AgCl$; conc. dissolves $AgBr$; AgI never.

Watch out!

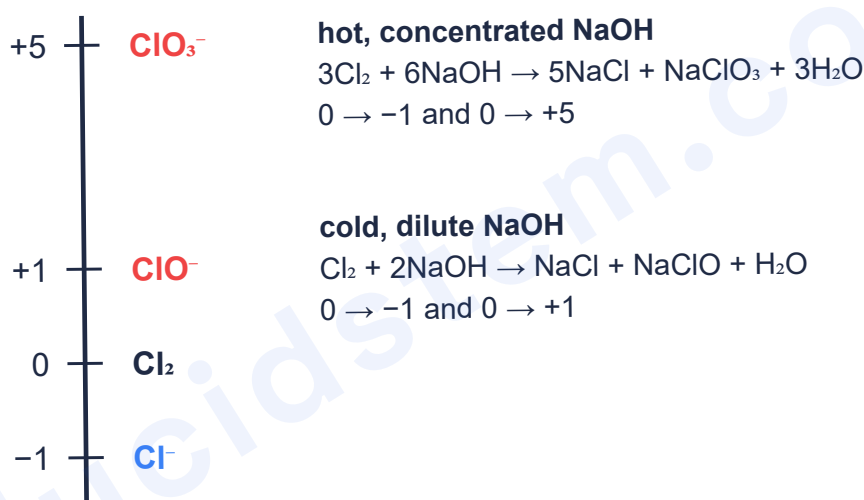
Chloride ions are too weak a reducing agent to reduce concentrated sulfuric acid, so no chlorine forms; the only product is HCl. The further the sulfur is reduced, the stronger the reducing agent: iodide takes sulfur all the way to -2 in H_2S . In the silver nitrate test, always acidify with **nitric** acid, never hydrochloric.

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4 Chlorine: disproportionation and water treatment

Syllabus 11.4

Disproportionation is a redox reaction in which the same element is simultaneously oxidised and reduced. Chlorine (oxidation number 0) disproportionates in sodium hydroxide: in **cold, dilute** NaOH it forms NaCl (-1) and NaClO (+1), the mixture used as bleach; in **hot, concentrated** NaOH it forms NaCl (-1) and NaClO₃ (+5). With water, $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO}$, and the chloric(I) acid kills bacteria, which is why chlorine is used to treat drinking water.



disproportionation: chlorine is oxidised and reduced at the same time

Fig. 1: oxidation numbers of chlorine in its reactions with sodium hydroxide

One element, two directions.

- ✓ **Cold dilute NaOH:** $\text{NaCl} + \text{NaClO}$ (-1 and +1).
- ✓ **Hot conc. NaOH:** $\text{NaCl} + \text{NaClO}_3$ (-1 and +5).
- ✓ **Water:** $\text{HCl} + \text{HClO}$; HClO kills bacteria.
- ✓ **Risk:** chlorinated organic compounds.

Watch out!

In disproportionation the **same element** is both oxidised and reduced, so chlorine appears in two products with different oxidation numbers. Do not mix up the two NaOH conditions: cold dilute gives chlorate(I), NaClO ; hot concentrated gives chlorate(V), NaClO_3 .

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