Group 17

Colours and volatility of the halogens, their oxidising power, reactions with hydrogen, hydrogen halide stability, reactions of halide ions with silver nitrate and concentrated sulfuric acid, and the reactions of chlorine with alkali and water.

11.1 Physical properties of the Group 17 elements

Element	Colour and state at room temperature
Chlorine, Cl_2	pale yellow-green gas
Bromine, Br_2	red-brown liquid (orange-brown vapour)
Iodine, I_2	grey-black solid (purple vapour)

- **Volatility decreases** down the group: boiling points increase. The molecules become larger with more electrons, so the **instantaneous dipole–induced dipole forces** between them are stronger and more energy is needed to separate them.
- The **bond strength of the X–X bond decreases** from Cl_2 to I_2 (the bonding pair is further from the nuclei and shielded by more electrons, so the attraction is weaker; F_2 is unusually weak because of lone-pair repulsion).

Intermolecular attractions and bond breaking are separate

Boiling a halogen separates X_2 molecules; it does not split them into atoms. Its boiling-point trend is therefore explained by **intermolecular dispersion forces**, not the covalent X–X bond energy. Down the group larger electron clouds are more polarizable, strengthening these attractions. The weakening X–X bond is relevant to chemical reactions, a different process.

Worked comparison: iodine is a solid at room temperature while chlorine is gaseous because considerably more energy is needed to overcome attractions between I_2 molecules. This does not mean an I–I bond is stronger than a Cl–Cl bond. Always state which attraction is being overcome.

> **TRY IT**
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> Why does iodine vapour remain purple rather than becoming a gas of isolated iodine atoms when iodine sublimes?

Answer: Sublimation mainly separates I_2 molecules from one another. Their covalent I–I bonds remain, so the vapour is molecular iodine.

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11.2 The chemical properties of the halogen elements and the hydrogen halides

Oxidising power

The halogens are **oxidising agents**, and the **oxidising power decreases down the group** ($Cl_2 > Br_2 > I_2$). Each halogen displaces a less reactive one from a solution of its halide:

$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$ $\quad$ $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

Observation: chlorine water turns a bromide solution orange and an iodide solution brown.

Reaction with hydrogen

$H_2 + F_2 \rightarrow 2HF$ explodes even in the dark. $H_2 + Cl_2 \rightarrow 2HCl$ explodes in sunlight. $H_2 + Br_2 \rightarrow 2HBr$ is slower and needs heating. $H_2 + I_2 \rightleftharpoons 2HI$ is slow, reversible and only partial. The reactivity decreases down the group because the **H–X bond** formed gets weaker, so less energy is released.

Thermal stability of the hydrogen halides

Stability **decreases down the group**: HCl is very stable, HI decomposes on heating. The **H–X bond becomes longer and weaker**, so less energy is needed to break it.

Predicting a displacement from electron transfer

A halogen acts as an oxidising agent by gaining electrons, $X_2 + 2e^- \rightarrow 2X^-$. Chlorine can accept electrons from bromide or iodide; iodine cannot normally oxidise chloride under the same aqueous conditions. The reverse sequence applies to the reducing ability of halide ions. Do not compare the oxidising power of Cl_2 with the reducing power of Cl^- as though they were the same species.

Worked example: add bromine water to potassium iodide. The ionic equation is $Br_2 + 2I^- \rightarrow 2Br^- + I_2$. Potassium ions are spectators. Brown aqueous iodine, or violet iodine in a suitable non-polar solvent layer, supports the reaction. Adding bromine to chloride does not give the analogous displacement; the original bromine colour may remain.

For hydrogen halides, the decreasing H–X bond strength makes thermal decomposition easier down the group. Distinguish a hydrogen halide gas from its aqueous acid: the gas consists mainly of molecules, while water enables ionisation. A trend in thermal stability is about bond breaking and does not by itself state the concentration or pH of an aqueous sample.

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Write the half-equations showing why chlorine is the oxidising agent in its reaction with iodide.

Answer: $Cl_2 + 2e^- \rightarrow 2Cl^-$ and $2I^- \rightarrow I_2 + 2e^-$. Chlorine gains electrons while iodide loses them; electrons cancel when the equations are added.

11.3 Some reactions of the halide ions

Reducing power

The halide ions act as **reducing agents**, and the **reducing power increases down the group** ($I^- > Br^- > Cl^-$), as the larger ion loses an electron more easily.

Reaction with concentrated sulfuric acid

- $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ (steamy white fumes of HCl). Cl^- is too weak a reducing agent to reduce the acid.
- $NaBr$ also gives HBr, but HBr then reduces some H_2SO_4: $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$ (orange-brown Br_2 and choking SO_2).
- NaI reduces the sulfur further, to SO_2, solid **sulfur** (yellow) and even H_2S (rotten-egg smell): $8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$, giving purple iodine vapour.

Test with silver nitrate

Acidify with dilute nitric acid, add aqueous silver nitrate, then aqueous ammonia:

Halide	Precipitate	Dilute $NH_3(aq)$	Concentrated $NH_3(aq)$
Cl^-	white $AgCl$	dissolves	dissolves
Br^-	cream $AgBr$	insoluble	dissolves
I^-	yellow AgI	insoluble	insoluble

$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$. (You do not need the formula of the $[Ag(NH_3)_2]^+$ complex.) The solubility in ammonia decreases from AgCl to AgI.

Separating acid–base and redox steps with sulfuric acid

The initial reaction of a solid sodium halide with concentrated sulfuric acid can produce a hydrogen halide by acid–base chemistry. For bromide and iodide, subsequent electron transfer reduces sulfur from +6 to

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lower oxidation states. The halide is oxidised to the halogen. Chloride is too weak a reducing agent for the comparable redox step, so observing HCl fumes is not evidence that sulfuric acid was reduced.

For sulfur dioxide sulfur is +4, for sulfur it is 0, and for hydrogen sulfide it is −2. The greater reducing power of iodide permits deeper reductions. Several products can coexist, so avoid presenting one balanced equation as a guarantee of a pure single product in the test mixture.

Worked example: in $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$, two bromides each lose one electron. Sulfur gains two electrons as it changes +6 to +4. In the hydrogen-sulfide equation, sulfur gains eight electrons, matching oxidation of eight iodides to four iodine molecules.

A defensible silver-halide identification

Use separate portions where other tests might introduce contaminating ions. Acidify with **nitric** acid before silver nitrate: hydrochloric acid would supply chloride and produce a false positive. The acid removes carbonate or hydroxide interferences. Record precipitate colour, then test ammonia solubility; a colour judgement alone is less reliable for pale or mixed precipitates.

Silver chloride dissolves in dilute ammonia because complex formation removes free silver ions and shifts dissolution equilibrium. Silver bromide requires more concentrated ammonia, whereas silver iodide remains insoluble under the usual test conditions. Dissolving a precipitate and bleaching a coloured solution are different observations; use precise wording.

> **TRY IT**
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> A cream precipitate forms after acidification and silver nitrate addition. It remains in dilute ammonia but dissolves in concentrated ammonia. Identify the halide.

Answer: Bromide, through formation of AgBr. Both colour and ammonia behaviour support the identification. The reagent must not have introduced bromide itself.

11.4 The reactions of chlorine

Chlorine with sodium hydroxide: disproportionation

- **Cold, dilute** NaOH: $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$. Chlorine goes from 0 to −1 (in Cl^-) and to **+1** (in ClO^-).
- **Hot, concentrated** NaOH: $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$. Chlorine goes from 0 to −1 and to **+5** (in ClO_3^-).

Both are **disproportionation** reactions: the same element is oxidised and reduced.

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Chlorine in water purification

Chlorine reacts with water: $Cl_2 + H_2O \rightleftharpoons HCl + HOCl$ (or $HClO$). The **chloric(I) acid** $HOCl$ and its ion ClO^- are the **active species** that kill bacteria. Adding chlorine to water is cheap and effective, but has risks (toxic chlorine, possible chlorinated organic compounds).

> **Use the correct colour and state names: chlorine pale green gas, bromine red-brown liquid, iodine grey-black solid; in non-polar solvents bromine is orange and iodine is violet.**

Why conditions change the disproportionation products

Cold dilute alkali gives chlorate(I), while hot concentrated alkali gives chlorate(V). Determine the oxidation number before naming the product. ClO^- contains chlorine +1; ClO_3^- contains chlorine +5. Both also produce chloride, −1. The hot reaction's 5 : 1 chloride-to-chlorate(V) ratio balances electrons: one chlorine loses five electrons while five chlorines each gain one.

Worked calculation: for complete cold-alkali reaction, 0.0200 mol Cl_2 consumes 0.0400 mol NaOH and produces 0.0200 mol each NaCl and NaClO. Under hot concentrated conditions, the same chlorine amount would give $0.0200/3 = 0.00667$ mol $NaClO_3$ according to the stated equation, not 0.0200 mol.

Water treatment balances the benefit of reducing waterborne infection against controlled risks from chlorine handling and reaction by-products. Explain the disinfecting species through the equilibrium producing HOCl and its conjugate base, rather than claiming dissolved chloride ions sterilise water. Chlorine and chloride are chemically different.

> TRY IT
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> Is chlorine's reaction with water disproportionation? Use oxidation numbers.

Answer: Yes. Chlorine starts at 0 in Cl_2 and becomes −1 in HCl and +1 in HOCl. The same starting element is reduced and oxidised.

Chapter check: distinguish halogen from halide, intermolecular attraction from covalent bond energy, and acid–base gas formation from the later redox step. Use **oxidation-number methods** to check all equations.

References and further reading

Scope follows section 11 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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