

# Group 17

AS

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## What you need to know

By the end of this topic you should be able to do the following for chlorine, bromine and iodine (the halogens, Group 17) and their compounds:

1. **Colours and volatility.** State the colour of each element and how volatility changes down the group.
2. **Bond strength.** Describe the trend in the strength of the Cl–Cl, Br–Br and I–I bonds, and explain it.
3. **Why volatility changes.** Explain the volatility trend using instantaneous dipole–induced dipole (id–id) forces between the molecules.
4. **Oxidising power.** Describe how strongly each halogen acts as an oxidising agent, and use this to predict displacement reactions.
5. **Reactions with hydrogen.** Describe how each halogen reacts with hydrogen and explain why the reactivity falls down the group.
6. **Hydrogen halides on heating.** Describe how the thermal stability of HCl, HBr and HI changes, and explain it with bond strengths.
7. **Halide ions as reducing agents.** Describe how strongly  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  act as reducing agents.
8. **Tests on halide ions.** Describe and explain what happens when halide ions react with aqueous silver ions and then aqueous ammonia (you do not need the formula of the silver–ammonia complex), and with concentrated sulfuric acid, with balanced equations.
9. **Chlorine with sodium hydroxide.** Describe the reactions of chlorine with cold and with hot aqueous sodium hydroxide, use oxidation numbers to explain them, and recognise them as disproportionation.
10. **Chlorine in water treatment.** Explain, with an equation, how chlorine purifies water by forming HOCl and  $\text{ClO}^-$ , which kill bacteria.

Fluorine and astatine are not in the list, but a question may ask you to predict astatine's properties from the trends.

## Understand it

### Three halogens, one pattern

Chlorine, bromine and iodine all have seven outer electrons ( $ns^2 np^5$ ). They exist as diatomic molecules,  $X_2$ , held together by one covalent bond, and each atom needs one more electron to fill its outer shell. Going down the group, each atom has one more shell of electrons, so:

- the atoms get **larger** and the X–X bond gets **longer**;
- the outer electrons are **further from the nucleus** and more **shielded** by the inner shells;
- each molecule has **more electrons** in total.

Almost everything in this topic follows from those three facts.

|                           | chlorine                  | bromine                         | iodine                            |
|---------------------------|---------------------------|---------------------------------|-----------------------------------|
| state at room temperature | gas                       | liquid                          | solid                             |
| colour of the element     | pale green (yellow-green) | red-brown (orange-brown vapour) | grey-black, shiny (purple vapour) |
| colour in water           | very pale green           | orange (yellow when dilute)     | brown                             |
| colour in hexane          | very pale green           | orange-red                      | purple (violet)                   |
| boiling point / °C        | –34                       | 59                              | 184                               |

### Volatility and id–id forces

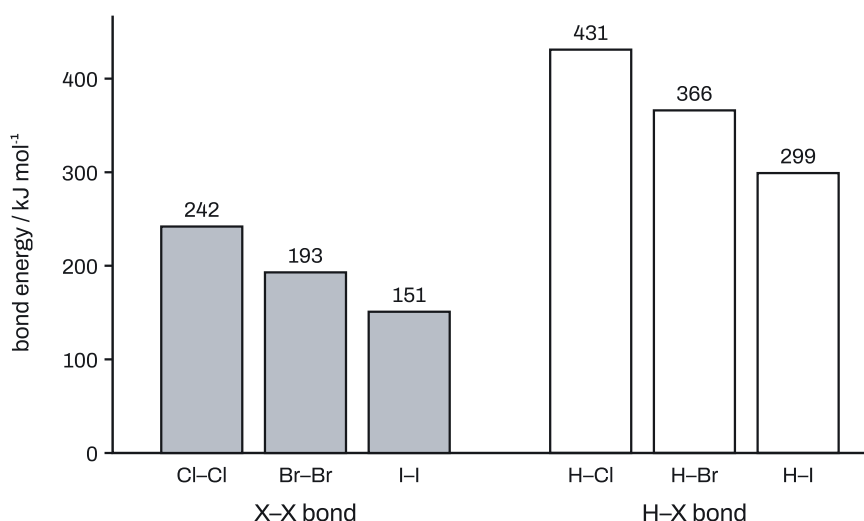
A **volatile** substance is one that turns into a vapour **easily**, at a low temperature. The halogens become **less volatile** down the group: chlorine is a gas, bromine a liquid, iodine a solid.

The halogens are simple molecules, so boiling one only separates molecules from each other; no covalent bonds break. The forces between the molecules are **instantaneous dipole–induced dipole (id–id) forces** (also called London or van der Waals' forces). Electrons are always moving, so at any instant one side of a molecule can have slightly more electron density than the other. That temporary dipole pushes on the electrons of the next molecule and induces a dipole in it, and the two attract.

A molecule with **more electrons** forms bigger temporary dipoles, so the id–id forces are **stronger**.  $I_2$  has 106 electrons,  $Br_2$  70 and  $Cl_2$  34, so iodine needs the most energy to separate its molecules and is the least volatile.

The explanation is **only** about the number of electrons and the id–id forces. Electronegativity, the X–X bond and the attraction of the nucleus for the outer electrons have nothing to do with volatility, and halogen molecules have no permanent dipole.

## Bond strength of X-X and H-X



Both the halogen-halogen bond and the hydrogen-halogen bond get **weaker** down the group. In a covalent bond the two nuclei attract the shared pair of electrons between them. Down the group:

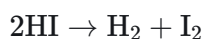
- the atom is larger, so the bond is **longer** and the shared pair is **further** from the halogen's nucleus;
- there are more inner shells, so there is **more shielding**;
- the larger, more diffuse orbitals **overlap less** well.

So the attraction between the nuclei and the bonding pair is weaker, and less energy is needed to break the bond.

## Thermal stability of the hydrogen halides

**Thermal stability** is how well a compound resists breaking down when heated.  $2\text{HX} \rightarrow \text{H}_2 + \text{X}_2$  needs the H-X bond to break, and the H-X bond gets weaker down the group, so:

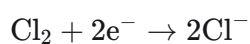
- HCl is the most stable: it does not decompose even at high temperatures;
- HBr decomposes a little on strong heating;
- HI decomposes easily: push a red-hot wire or glass rod into HI and **purple fumes** of iodine appear.



Thermal stability is about the **H-X bond energy**. It is not about the electronegativity of X and not about the X-X bond.

## Halogens as oxidising agents

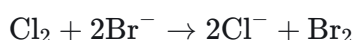
A halogen reacts by **gaining electrons** to become halide ions, so halogens are **oxidising agents** (they take electrons from something else):



Chlorine is the strongest oxidising agent and iodine the weakest: **oxidising power**  $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ . A chlorine atom is the smallest, so an incoming electron comes closest to the nucleus and is least shielded from it. It is attracted most strongly, and chlorine gains electrons most readily.

A halogen reacts with metals too, for example  $2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3$ : iron loses electrons and chlorine gains them.

**Displacement.** A halogen oxidises the halide ions of any halogen **below** it. Add chlorine water to potassium bromide solution and the chlorine takes electrons from the bromide ions:



The solution turns from colourless to orange (the bromine). A halogen does **not** react with halide ions of a halogen above it: iodine added to bromide ions gives no reaction, because iodine is a weaker oxidising agent than bromine.

| added to                 | $\text{Cl}^-(\text{aq})$ | $\text{Br}^-(\text{aq})$    | $\text{I}^-(\text{aq})$   |
|--------------------------|--------------------------|-----------------------------|---------------------------|
| $\text{Cl}_2(\text{aq})$ | no reaction              | orange: $\text{Br}_2$ forms | brown: $\text{I}_2$ forms |
| $\text{Br}_2(\text{aq})$ | no reaction              | no reaction                 | brown: $\text{I}_2$ forms |
| $\text{I}_2(\text{aq})$  | no reaction              | no reaction                 | no reaction               |

Bromine and iodine solutions can look alike (both yellow-brown when dilute), so shake the mixture with **hexane**: the halogen moves into the hexane layer on top, which turns **orange-red** for bromine and **purple** for iodine.

## Halide ions as reducing agents

The same story runs backwards. A halide ion that gives up its electron easily is a good **reducing agent**. The iodide ion is the largest, so its outer electrons are furthest from the nucleus, most shielded and lost most easily. **Reducing power**  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ , the opposite order to the halogens' oxidising power.

## Reactions with hydrogen

Each halogen reacts with hydrogen to form the hydrogen halide,  $\text{H}_2 + \text{X}_2 \rightarrow 2\text{HX}$ , but they get less reactive down the group:

### halogen reaction with hydrogen

|          |                                                                                                                               |
|----------|-------------------------------------------------------------------------------------------------------------------------------|
| chlorine | explosive in sunlight or with a flame; the green colour disappears                                                            |
| bromine  | needs heating (with a platinum catalyst); the orange-brown colour fades                                                       |
| iodine   | slow even when heated; <b>reversible</b> , so it never goes to completion; the purple vapour fades but does not all disappear |

Two reasons go together: the oxidising power of the halogen falls, and the H–X bond formed is weaker, so less energy is released (the reaction is less exothermic).

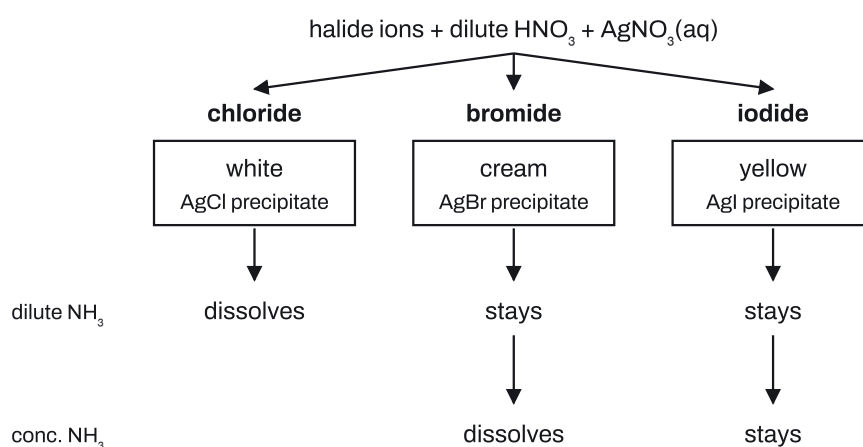
## Halide ions and silver ions

Adding aqueous silver nitrate to a solution of halide ions (acidified with dilute nitric acid first) gives a **precipitate** of the silver halide:



Then add aqueous ammonia to see whether the precipitate dissolves. The silver halides get **less soluble** in ammonia down the group:

| halide   | precipitate with $\text{Ag}^+(\text{aq})$ | + dilute $\text{NH}_3(\text{aq})$ | + concentrated $\text{NH}_3(\text{aq})$ |
|----------|-------------------------------------------|-----------------------------------|-----------------------------------------|
| chloride | white                                     | dissolves (colourless solution)   | dissolves                               |
| bromide  | cream (off-white)                         | does not dissolve                 | dissolves                               |
| iodide   | yellow                                    | does not dissolve                 | does not dissolve                       |

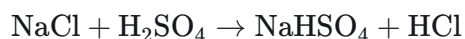


Solubility in ammonia falls:  $\text{AgCl} > \text{AgBr} > \text{AgI}$ .

The colours are close, so the ammonia step is what really tells chloride, bromide and iodide apart.

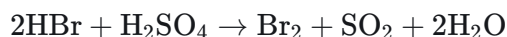
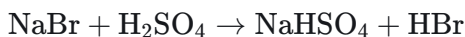
## Halide ions and concentrated sulfuric acid

Warm a solid sodium halide with concentrated sulfuric acid. **Every** halide first takes part in an **acid–base** reaction: the acid gives a proton to the halide ion, forming the hydrogen halide, which appears as **steamy (misty) fumes** in moist air.

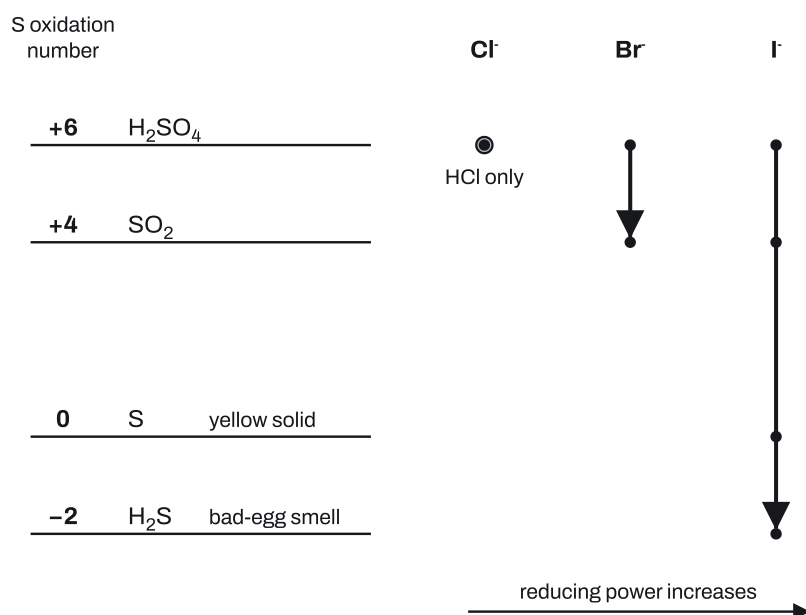
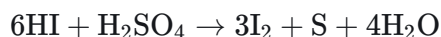
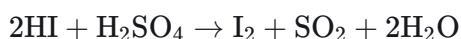
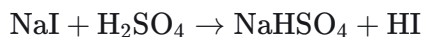


What happens next depends on how good a reducing agent the halide is. Concentrated sulfuric acid is also an oxidising agent (sulfur is at +6).

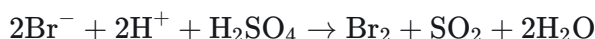
- **Chloride** is too weak a reducing agent to reduce the acid. The reaction stops at HCl: acid–base only, and the sulfur stays at **+6**.
- **Bromide** is strong enough to reduce the acid to sulfur dioxide (sulfur **+6 to +4**) and is oxidised to bromine: acid–base, then redox. You see steamy fumes, then **orange-brown fumes** of bromine; SO<sub>2</sub> is a colourless gas.



- Iodide** is the strongest reducing agent and reduces the sulfur much further: to  $\text{SO}_2$  (+4), to sulfur (**0**, a **yellow solid**) and to hydrogen sulfide (**-2**, a gas that smells of bad eggs). It is oxidised to iodine: a **grey-black solid** and **purple fumes**. Only a little steamy HI is seen, because most of it is oxidised.



The redox steps can also be written with the halide ion. Each  $\text{Br}^-$  gives one electron and sulfur needs two to go from +6 to +4, so two bromide ions reduce one sulfur atom:



Count electrons the same way for iodide: to S (+6 to 0) needs 6 electrons, so 6 iodide ions per sulfur atom; to  $\text{H}_2\text{S}$  (+6 to -2) needs 8.

## Chlorine with sodium hydroxide: disproportionation

**Disproportionation** is a reaction in which **the same element** in one species is **both oxidised and reduced**. Chlorine starts at 0 and ends up in two products, one with a lower and one with a higher oxidation number.

**Cold, dilute** sodium hydroxide (about 15 °C) gives sodium chloride and sodium chlorate(I), which is bleach:



Chlorine goes from 0 to -1 in NaCl (reduced) and from 0 to +1 in NaClO (oxidised). As an ionic equation:



**Hot, concentrated** sodium hydroxide (about 70 °C) gives sodium chloride and sodium chlorate(V):

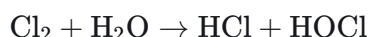


Chlorine goes from 0 to -1 in NaCl and from 0 to **+5** in NaClO<sub>3</sub>. The electrons balance: one chlorine atom losing 5 electrons provides the electrons for five atoms gaining one each, which is why the ratio of chloride to chlorate(V) is 5 : 1.

In fact the chlorate(I) made first disproportionates itself when warm:  $3\text{NaClO} \rightarrow 2\text{NaCl} + \text{NaClO}_3$  (Cl +1 goes to -1 and +5). The same patterns work for bromine and potassium hydroxide.

## Chlorine in water purification

A little chlorine added to drinking water reacts with it. This is also a disproportionation (Cl 0 to -1 in HCl and 0 to +1 in HOCl):



Chloric(I) acid, HOCl, partly ionises to chlorate(I) ions:  $\text{HOCl} \rightleftharpoons \text{H}^+ + \text{ClO}^-$ . **HOCl and ClO<sup>-</sup>** (chlorine at +1) are the active species: they **kill bacteria** and other microorganisms, making the water safe to drink.

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## Key facts and formulas

"Given" means it is printed in the 9701 Data Booklet or on the paper's Periodic Table. "Learn it" means you must remember it. The Data Booklet does not print equations, colours or observations.

| Formula                                                                                                                                                                                                                           | Status   |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| Relative atomic masses: Cl 35.5, Br 79.9, I 126.9, Na 23.0, K 39.1, Ag 107.9, O 16.0                                                                                                                                              | Given    |
| Bond energies: Cl-Cl 242, Br-Br 193, I-I 151, H-Cl 431, H-Br 366, H-I 299, H-H 436 kJ mol <sup>-1</sup>                                                                                                                           | Given    |
| Molar volume of a gas = 24.0 dm <sup>3</sup> mol <sup>-1</sup> at room conditions                                                                                                                                                 | Given    |
| Colours: Cl <sub>2</sub> pale green gas, Br <sub>2</sub> red-brown liquid, I <sub>2</sub> grey-black solid (purple vapour)                                                                                                        | Learn it |
| Down the group: volatility ↓ (id-id forces ↑, more electrons); X-X and H-X bond strength ↓; HX thermal stability ↓                                                                                                                | Learn it |
| Oxidising power Cl <sub>2</sub> > Br <sub>2</sub> > I <sub>2</sub> ; reducing power I <sup>-</sup> > Br <sup>-</sup> > Cl <sup>-</sup>                                                                                            | Learn it |
| Displacement: Cl <sub>2</sub> + 2I <sup>-</sup> → 2Cl <sup>-</sup> + I <sub>2</sub>                                                                                                                                               | Learn it |
| Silver halides: AgCl white (dissolves in dilute NH <sub>3</sub> ), AgBr cream (dissolves in concentrated NH <sub>3</sub> ), AgI yellow (insoluble)                                                                                | Learn it |
| With concentrated H <sub>2</sub> SO <sub>4</sub> : Cl <sup>-</sup> gives HCl only; Br <sup>-</sup> gives HBr, Br <sub>2</sub> , SO <sub>2</sub> ; I <sup>-</sup> gives HI, I <sub>2</sub> , SO <sub>2</sub> , S, H <sub>2</sub> S | Learn it |

| Formula                                                                                                                     | Status   |
|-----------------------------------------------------------------------------------------------------------------------------|----------|
| Cold NaOH: $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$ (Cl 0 to -1 and +1)     | Learn it |
| Hot NaOH: $3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$ (Cl 0 to -1 and +5) | Learn it |
| Water: $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$ ; HOCl and $\text{ClO}^-$ kill bacteria      | Learn it |
| $n = \frac{m}{M_r}$ ; $n = c \times V$ ; gas volume = $n \times 24.0 \text{ dm}^3$                                          | Learn it |

Formula masses you will use often: NaCl 58.5, NaBr 102.9, NaI 149.9, KCl 74.6, KClO 90.6, NaClO<sub>3</sub> 106.5, AgCl 143.4, AgBr 187.8, AgI 234.8.

## How to do it

In the Paper 1 and Paper 2 questions we have tagged for this topic (104 questions, 2021–2025), the types came up this often. 29 of the 104 questions mix more than one type, so the counts add up to 157.

| Question type                                        | Questions |
|------------------------------------------------------|-----------|
| Halide ions with concentrated sulfuric acid          | 29        |
| Chlorine with cold or hot sodium hydroxide           | 25        |
| Halogens as oxidising agents and displacement        | 22        |
| Silver nitrate then ammonia test                     | 21        |
| Physical properties: colours, states, volatility     | 14        |
| Choose the correct statement across several trends   | 14        |
| Bond strengths and hydrogen halide thermal stability | 9         |
| Chlorine in water purification                       | 9         |
| Calculations in halogen reactions                    | 7         |
| Halogens with hydrogen                               | 4         |
| Other halogen redox: oxidation numbers and equations | 3         |

### 1. Halide ions with concentrated sulfuric acid (29 questions)

- Write the acid–base step first**, for every halide:  $\text{NaX} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HX}$  (steamy fumes). The sodium product is NaHSO<sub>4</sub>, not "NaSO<sub>4</sub>".
- Decide how far the redox goes**, from the halide's reducing power: chloride none; bromide to SO<sub>2</sub>; iodide to SO<sub>2</sub>, S and H<sub>2</sub>S.

3. **Give the sulfur oxidation numbers** if asked:  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_4^-$  +6,  $\text{SO}_2$  +4, S 0,  $\text{H}_2\text{S}$  -2.
4. **Match observations to species:** steamy fumes =  $\text{HX}$ ; orange-brown fumes =  $\text{Br}_2$ ; grey-black solid or purple fumes =  $\text{I}_2$ ; yellow solid = S; bad-egg smell =  $\text{H}_2\text{S}$ .
5. **Explain** with reducing power: "iodide ions are larger, so the outer electron is further from the nucleus and more shielded, so it is lost more easily; iodide is a stronger reducing agent and reduces the sulfuric acid further."

#### Variations you will meet:

- **"Name the type of reaction"** for each salt: NaCl is acid–base only; NaBr and NaI are acid–base then redox.
- **Identify the halide from one clue:**  $\text{H}_2\text{S}$  or a yellow solid means iodide; the lowest sulfur oxidation number being +4 means bromide; no change in sulfur's oxidation number means chloride.
- **Ionic redox equations**, such as  $2\text{Br}^- + 2\text{H}^+ + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$ . Balance electrons: sulfur's drop in oxidation number equals the number of halide ions oxidised (2 for  $\text{SO}_2$ , 6 for S, 8 for  $\text{H}_2\text{S}$ ).
- **Why concentrated sulfuric acid is used to make HCl but not HBr or HI:** the HBr and HI formed are oxidised by the acid, so the product is impure and the yield is low.
- **Reagent chains** that combine this with the silver test, for example a precipitate that stays in ammonia and gives purple fumes with the acid is AgI.

## 2. Chlorine with cold or hot sodium hydroxide (25 questions)

1. **Read the conditions.** Cold and dilute: chloride and chlorate(I),  $\text{ClO}^-$ . Hot and concentrated: chloride and chlorate(V),  $\text{ClO}_3^-$ .
2. **Write the equation:**  $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$ , or  $3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$ .
3. **Give the oxidation numbers** of chlorine: 0 in  $\text{Cl}_2$ ; -1 in  $\text{Cl}^-$ ; +1 in  $\text{ClO}^-$ ; +5 in  $\text{ClO}_3^-$ .
4. **Say why it is disproportionation:** chlorine is both oxidised (0 to +1 or +5) and reduced (0 to -1) in the same reaction. Quote the numbers, not just the definition.

#### Variations you will meet:

- **Which conditions give a +5 compound?** Hot concentrated NaOH. Cold dilute NaOH gives +1.
- **Other halogens and bases:** bromine with KOH gives KBr and KBrO (cold) or KBr and  $\text{KBrO}_3$  (hot). Treat them exactly like chlorine.
- **A product that reacts further**, such as  $3\text{KBrO} \rightarrow 2\text{KBr} + \text{KBrO}_3$  or  $4\text{KClO}_3 \rightarrow 3\text{KClO}_4 + \text{KCl}$ : if one element goes both up and down, it is disproportionation.
- **Balancing with letters** ( $x\text{Cl}_2 + 6\text{NaOH} \rightarrow y\text{NaCl} + z\text{NaClO}_3 + \dots$ ): balance the electrons (5 up for each chlorate, 1 down for each chloride), then sodium. The sodium ions are spectators, so their concentration stays the same if the volume does.
- **Match a formula to a percentage by mass:** work out the percentage of oxygen in NaClO and  $\text{NaClO}_3$  and see which fits; then name the conditions that make it.

### 3. Halogens as oxidising agents and displacement (22 questions)

1. **Place both halogens in the order**  $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .
2. **The higher one displaces the lower one's halide.** If the halogen added is lower (or the same), there is no reaction.
3. **Write the ionic equation** without spectator ions:  $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$ , not with  $\text{Na}^+$  or  $\text{K}^+$ .
4. **Observation:** the colour of the halogen formed (orange for  $\text{Br}_2$ , brown for  $\text{I}_2$  in water; orange-red or purple in hexane).
5. **Explain:** the halogen added is the stronger oxidising agent; it gains electrons from the halide ions, which are oxidised. Say which **ions** lose electrons: the iodide ions, not "the iodine".

#### Variations you will meet:

- **A grid of results for unknown halogens U, V, W:** the halogen that displaces both others is the strongest oxidising agent; its ion is the weakest reducing agent. Reverse the order for the ions.
- **Hydrogen halides as the source of halide ions**, such as  $\text{HBr(aq)}$ : it behaves exactly like  $\text{KBr(aq)}$ .
- **"Redox and displacement"** both describe  $\text{Cl}_2 + 2\text{NaBr} \rightarrow 2\text{NaCl} + \text{Br}_2$ ; it is not disproportionation, because two different elements change oxidation number.
- **Chlorine with a metal:**  $2\text{Al} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3$ ; the halogen gains electrons from the metal.
- **Predict a heavier halogen** (astatine, tennessine): an even weaker oxidising agent, so it displaces none of the others.

### 4. Silver nitrate then ammonia test (21 questions)

1. **Give the precipitate colour and the word "precipitate":** white  $\text{AgCl}$ , cream  $\text{AgBr}$ , yellow  $\text{AgI}$ .
2. **Then the ammonia:**  $\text{AgCl}$  dissolves in dilute;  $\text{AgBr}$  only in concentrated;  $\text{AgI}$  in neither.
3. **Equation if asked:**  $\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}$  (state symbols (aq), (aq), (s)).

#### Variations you will meet:

- **Mixtures of silver halides** shaken with ammonia: the solid left behind is the least soluble one; the dissolved one comes back as a precipitate when the solution is acidified.
- **Salts of other metals**, such as  $\text{MgBr}_2$  or  $\text{CaCl}_2$ : two halide ions per formula, so one mole of salt gives two moles of  $\text{AgX}$ .
- **Which reagent dissolves the precipitate** from  $\text{AgNO}_3$  and  $\text{NaCl}$ : aqueous ammonia, not an acid.
- **Order the solubilities** (or equilibrium constants for  $\text{AgX(s)} \rightleftharpoons \text{Ag}^+ + \text{X}^-$ ):  $\text{AgCl} > \text{AgBr} > \text{AgI}$ .

### 5. Physical properties: colours, states, volatility (14 questions)

1. **State the colours and states** from the table in "Understand it".
2. **Volatility decreases down the group** (boiling point increases).
3. **Explain** in three linked steps: more electrons in the molecule; stronger id-id forces between molecules; more energy needed to separate them.

**Variations you will meet:**

- **Multiple-choice distractors** blame the X–X bond energy, electronegativity or permanent dipoles. All wrong: the covalent bonds do not break on boiling.
- **"Define volatile"**: turns into a vapour easily (at a low temperature).
- **Predict astatine**: a black solid, even less volatile than iodine, with lower electronegativity.

**6. Choose the correct statement across several trends (14 questions)**

1. **Test each statement against its trend**, one by one, and then check that the **explanation** matches the statement.
2. Common traps: "iodine is the strongest oxidising agent" (it is the weakest); " $\text{Cl}^-$  is the strongest reducing agent" (it is the weakest); "iodine is a solid because its I–I bond is strong" (it is the weakest bond; the id–id forces explain it); "HI is more stable" (it is the least stable).
3. For **"which statements are correct"** questions, test each numbered statement separately; one wrong link makes the whole statement wrong.
4. **Deduce halogens from clues**: weaker X–X bond means further down; stronger id–id forces means further down; a stronger oxidising agent means further up.

**7. Bond strengths and hydrogen halide thermal stability (9 questions)**

1. **State the trend**: bond strength decreases from Cl to I (both X–X and H–X); HCl is the most thermally stable, HI the least.
2. **Explain** (usually 2 marks): the atom is larger / the bond is longer; so the bonding pair is further from the nucleus (with more shielding) and less strongly attracted, or the orbitals overlap less.
3. **Link to stability**: the weaker H–X bond needs less energy to break, so HX decomposes more easily.

**Variations you will meet:**

- **Heating with a hot wire**: HI gives purple fumes of iodine; HCl gives nothing.
- **Estimate a value for HBr** (bond energy, decomposition temperature or an equilibrium constant) that lies between the values for HCl and HI.
- **"Describe" and "explain" both** appear: give the trend and then the reason.

**8. Chlorine in water purification (9 questions)**

1. **Equation**:  $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$  (or with  $\text{H}^+ + \text{Cl}^-$  for HCl).
2. **Active species**: HOCl and  $\text{ClO}^-$ , chlorine at +1.
3. **Role**: they kill bacteria (microorganisms) in the water.

**Variations you will meet**: the change in chlorine's oxidation number (0 to +1 and 0 to –1); the use of HOCl (water treatment); how HOCl is made (chlorine added to water).

## 9. Calculations in halogen reactions (7 questions)

1. **Write the balanced equation** for the reaction in the question.
2. **Find moles** of what you know:  $n = \frac{m}{M_r}$ ,  $n = c \times V$  ( $V$  in  $\text{dm}^3$ ) or  $n = \frac{\text{gas volume}}{24.0}$ .
3. **Use the ratio** from the equation (for hot  $\text{NaOH}$ ,  $3\text{Cl}_2 : 6\text{NaOH} : 5\text{NaCl} : 1\text{NaClO}_3$ ; for cold,  $1 : 2 : 1 : 1$ ).
4. **Convert** to the quantity asked, with units, to 3 significant figures unless told otherwise.

**Variations you will meet:** percentage by mass of oxygen to identify a chlorate; concentration of  $\text{NaClO}$  in bleach from the volume of  $\text{O}_2$  it makes with hydrogen peroxide (remember any dilution factor); mass of a silver halide precipitate.

## 10. Halogens with hydrogen (4 questions)

1. **Describe:** chlorine reacts explosively in sunlight; bromine needs heating; iodine reacts slowly and reversibly.
2. **Explain:** down the group the  $\text{H-X}$  bond formed is weaker (and the halogen is a weaker oxidising agent), so the reaction is less vigorous and less exothermic.
3. **Observation** for iodine vapour with hydrogen: the purple colour fades.

## 11. Other halogen redox: oxidation numbers and equations (3 questions)

1. **Assign oxidation numbers** with  $\text{O} = -2$  and  $\text{H} = +1$ , and remember the more electronegative halogen is negative in an interhalogen: in  $\text{ICl}$ ,  $\text{Cl}$  is  $-1$  and  $\text{I}$  is  $+1$ .
2. **See what goes up and what goes down**, then balance electrons before atoms.

For example, chlorate(I) oxidises chloride ions in acid ( $\text{Cl} +1$  and  $-1$  both go to  $0$ ):  $\text{ClO}^- + \text{Cl}^- + 2\text{H}^+ \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ .

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## Worked examples

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The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

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## Example 1

Use bond energies from the Data Booklet ( $\text{H-H}$  436,  $\text{Cl-Cl}$  242,  $\text{I-I}$  151,  $\text{H-Cl}$  431,  $\text{H-I}$  299  $\text{kJ mol}^{-1}$ ).

(a) Calculate the enthalpy change for  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$  and for  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ . [3]

(b) Use your answers to explain the difference in the reactivity of chlorine and iodine with hydrogen. [2]

(c) A red-hot glass rod is placed in a gas jar of each hydrogen halide. State and explain what is seen. [3]

(a) Bonds broken minus bonds made.

For HCl:  $436 + 242 = 678$  broken,  $2 \times 431 = 862$  made, so  $\Delta H = 678 - 862 = -184 \text{ kJ mol}^{-1}$ . **M1** (bonds broken minus bonds made) **A1**

For HI:  $436 + 151 = 587$  broken,  $2 \times 299 = 598$  made, so  $\Delta H = 587 - 598 = -11 \text{ kJ mol}^{-1}$ . **A1**

(b) Chlorine reacts explosively and iodine only slowly and reversibly. **B1** The H–Cl bond is much stronger than the H–I bond, so far more energy is released when HCl forms, and the reaction with chlorine is much more exothermic. **B1**

(c) Nothing happens in the hydrogen chloride; purple fumes (iodine) appear in the hydrogen iodide. **B1** The H–I bond is longer, so the bonding pair is further from the iodine nucleus and less strongly attracted; **B1** it is weaker ( $299$  against  $431 \text{ kJ mol}^{-1}$ ), so HI decomposes,  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ , and HCl is thermally stable. **B1**

## Example 2

Solid potassium bromide is warmed with concentrated sulfuric acid.

(a) Write equations for the two reactions that take place, and name the type of each. [3]

(b) Give the oxidation number of sulfur at the start and in the sulfur-containing product of the second reaction. [1]

(c) Describe two observations. [2]

(d) When potassium iodide is used instead, the sulfur ends up in a lower oxidation state. Name the product with the lowest oxidation number of sulfur, and explain why iodide can reduce the acid further than bromide can. [3]

(a)  $\text{KBr} + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{HBr}$ : acid–base. **B1**

$2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$  **B1**: redox. **B1**

(b) From  $+6$  in  $\text{H}_2\text{SO}_4$  to  $+4$  in  $\text{SO}_2$ . **B1**

(c) Steamy (misty) fumes of HBr; orange-brown fumes of bromine. **B1 B1**

(d) Hydrogen sulfide,  $\text{H}_2\text{S}$ , with sulfur at  $-2$ . **B1** An iodide ion is larger than a bromide ion, so its outer electrons are further from the nucleus and more shielded; **B1** it loses an electron more easily, so it is a stronger reducing agent. **B1**

### Example 3

Chlorine is bubbled into 250 cm<sup>3</sup> of cold 0.800 mol dm<sup>-3</sup> potassium hydroxide until all the KOH has reacted.

(a) Write an equation for the reaction and use oxidation numbers to explain why it is a disproportionation. **[3]**

(b) Calculate the volume of chlorine, measured at room conditions, that reacts. **[2]**

(c) Calculate the mass of potassium chlorate(I) formed. **[2]**

(d) The solution is then heated, and all the potassium chlorate(I) reacts:  $3\text{KClO} \rightarrow 2\text{KCl} + \text{KClO}_3$ .

Calculate the total mass of potassium chloride in the solution now. **[2]**

**(a)**  $\text{Cl}_2 + 2\text{KOH} \rightarrow \text{KCl} + \text{KClO} + \text{H}_2\text{O}$  **B1**

Chlorine goes from 0 in Cl<sub>2</sub> to -1 in KCl, so it is reduced, and from 0 to +1 in KClO, so it is oxidised. **M1** The same element is both oxidised and reduced. **A1**

**(b)**  $n(\text{KOH}) = 0.800 \times \frac{250}{1000} = 0.200 \text{ mol}$ , so  $n(\text{Cl}_2) = \frac{0.200}{2} = 0.100 \text{ mol}$ . **M1**

Volume =  $0.100 \times 24.0 = 2.40 \text{ dm}^3$ . **A1**

**(c)**  $n(\text{KClO}) = n(\text{Cl}_2) = 0.100 \text{ mol}$ .  $M_r(\text{KClO}) = 39.1 + 35.5 + 16.0 = 90.6$ . **M1**

Mass =  $0.100 \times 90.6 = 9.06 \text{ g}$ . **A1**

**(d)** 0.100 mol KClO gives  $\frac{2}{3} \times 0.100 = 0.0667 \text{ mol}$  more KCl, so the total is  $0.100 + 0.0667 = 0.1667 \text{ mol}$ . **M1**

Mass =  $0.1667 \times 74.6 = 12.4 \text{ g}$ . **A1**

### Example 4

A 1.920 g sample of a mixture of sodium chloride and sodium iodide is dissolved in water and acidified with dilute nitric acid. An excess of aqueous silver nitrate is added. The precipitate is filtered off, washed and dried: its mass is 4.042 g.

(a) Describe the appearance of the precipitate and what happens when it is then shaken with an excess of dilute aqueous ammonia. **[2]**

(b) Calculate the mass of sodium iodide in the sample and its percentage by mass. **[4]**

(c) Calculate the mass of solid left after the precipitate is shaken with excess dilute ammonia. **[1]**

**(a)** A mixture of white AgCl and yellow AgI: a pale yellow precipitate. **B1** With dilute ammonia the silver chloride dissolves and a yellow solid (AgI) remains. **B1**

**(b)** Let the sample contain  $a$  mol NaCl and  $b$  mol NaI. Each mole of salt gives one mole of silver halide. **M1**

$$58.5a + 149.9b = 1.920 \quad 143.4a + 234.8b = 4.042$$

**M1** for both equations with the right  $M_r$  values.

From the first,  $a = \frac{1.920 - 149.9b}{58.5}$ . Substituting and solving gives  $b = 0.00501$  mol and  $a = 0.0200$  mol. **M1**

Mass of NaI =  $0.00501 \times 149.9 = 0.751$  g, which is  $\frac{0.751}{1.920} \times 100 = 39.1\%$ . **A1**

(c) Only AgI is left:  $0.00501 \times 234.8 = 1.18$  g. **B1**

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## Common mistakes

- **Explaining volatility with bond strength or electronegativity.** Boiling a halogen breaks only the id-id forces between molecules. Examiners see answers about electronegativity or the nucleus attracting outer electrons every year; say "more electrons, stronger id-id forces".
- **Explaining thermal stability with electronegativity.** The reason is the H-X bond energy: longer, weaker H-I bond. Also don't mix up the halogens ( $X_2$ ) with the hydrogen halides (HX).
- **Showing a redox reaction for NaCl and concentrated sulfuric acid.** Chloride only gives the acid-base reaction,  $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$ . Write the formula  $\text{NaHSO}_4$  correctly.
- **Talking about the "oxidising power of the halides".** Halide ions are **reducing** agents; halogens are oxidising agents. The difference between NaCl, NaBr and NaI with sulfuric acid is explained by the halides' **reducing** power.
- **Wrong oxidation number of sulfur in  $\text{HSO}_4^-$ .** It is +6, the same as in  $\text{H}_2\text{SO}_4$ ; the acid-base step does not change it.
- **Not naming the fumes and solids.** A dark grey (black) solid from NaI is iodine; a yellow solid is sulfur; steamy fumes are the hydrogen halide.
- **Spectator ions in a displacement equation.** Write  $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$ , not with  $\text{Na}^+$ . When explaining, say the **iodide ions** lose electrons, not "iodine".
- **Defining disproportionation without using it.** Give the actual oxidation numbers of chlorine: 0 to -1 and 0 to +1 (cold) or +5 (hot). Chlorine in  $\text{ClO}_3^-$  is +5, not +1.
- **Colours of silver halides without "precipitate",** or calling AgBr "white". AgBr is cream; the ammonia step is what separates chloride from bromide.

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## How to get the marks

- **"Describe"** a trend: say which way it goes and between which elements ("volatility decreases from chlorine to iodine"). **"Explain"**: give the reason as a chain (bigger atom, further from nucleus, more shielding, weaker attraction).
- **"Describe and explain"**: two parts, two sets of marks. A trend with no reason, or a reason with no trend, gets half.
- **Observations** are what you see: colour and state ("orange-brown fumes", "yellow solid", "cream precipitate"). Naming the substance is not an observation unless the question asks for its identity too.

- **Equations:** balanced, correct formulae; use ionic equations when asked, without spectator ions. Add state symbols when the question asks for them.
- **Oxidation numbers** must have a sign: +5, not 5.
- **"Identify"** means name or formula; either is usually accepted, but a wrong formula loses the mark.
- **Calculations:** show the moles at each step, then give the answer to 3 significant figures with units. Method marks follow through from an earlier error.
- **Multiple-choice rows** with a statement and an explanation need both halves correct.

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## Quick check

1. State the colour of iodine as (a) a solid, (b) a vapour, (c) a solution in hexane. Which of chlorine, bromine and iodine is a liquid at room temperature?
2. Bromine water is added separately to aqueous potassium chloride and aqueous potassium iodide. Which reacts? Write the ionic equation and state what is seen when the mixture that reacts is shaken with hexane.
3. (a) Write an equation for the reaction of chlorine with water. (b) Give the oxidation number of chlorine in each chlorine-containing product. (c) Name the two species that kill bacteria.
4. Chlorine reacts with  $25.0 \text{ cm}^3$  of hot, concentrated  $3.00 \text{ mol dm}^{-3}$  potassium hydroxide until all the KOH is used up. Calculate the volume of chlorine used at room conditions and the mass of potassium chloride formed.
5. An aqueous potassium halide gives a cream precipitate with acidified silver nitrate. What happens when dilute ammonia, and then concentrated ammonia, is added? What would you see if the solid potassium halide were warmed with concentrated sulfuric acid?

## Answers

1. (a) Grey-black (shiny) solid. (b) Purple. (c) Purple (violet). Bromine is the liquid.
2. Only potassium iodide reacts, because bromine is a stronger oxidising agent than iodine but weaker than chlorine.  $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$ . The solution turns brown, and the hexane layer turns purple.
3. (a)  $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$ . (b) -1 in HCl and +1 in HOCl (a disproportionation). (c) HOCl and  $\text{ClO}^-$ .
4.  $3\text{Cl}_2 + 6\text{KOH} \rightarrow 5\text{KCl} + \text{KClO}_3 + 3\text{H}_2\text{O}$ .  $n(\text{KOH}) = 3.00 \times 0.0250 = 0.0750 \text{ mol}$ , so  $n(\text{Cl}_2) = 0.0375 \text{ mol}$  and the volume is  $0.0375 \times 24.0 = 0.900 \text{ dm}^3$ .  $n(\text{KCl}) = \frac{5}{6} \times 0.0750 = 0.0625 \text{ mol}$ , mass =  $0.0625 \times 74.6 = 4.66 \text{ g}$ .
5. It is a bromide. The cream precipitate ( $\text{AgBr}$ ) does not dissolve in dilute ammonia but does dissolve in concentrated ammonia. With concentrated sulfuric acid: steamy fumes ( $\text{HBr}$ ) and orange-brown fumes (bromine); sulfur dioxide also forms, a colourless gas.

## Past questions to try

- 9701/21/M/J/21 Q3: sodium chloride and sodium iodide with concentrated sulfuric acid, with equations.
- 9701/23/M/J/21 Q1: id-id forces, displacement observations, bleach and its reactions.
- 9701/12/F/M/25 Q19: ranking unknown halide ions as reducing agents from a grid of results.
- 9701/13/O/N/22 Q22: balancing chlorine with hot sodium hydroxide.