

# CAIE Chemistry A-level

## 11: Group 17 Notes

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## Physical Properties of the Group 17 Elements

The Group 17 elements are also known as the halogens.

### Colours and Trends in Volatility

At room temperature, the colours of the halogens get darker down the group. The boiling points also increase due to the increasing strength of the **intermolecular forces**.

- **Fluorine** - pale yellow gas
- **Chlorine** - green gas
- **Bromine** - red-brown liquid
- **Iodine** - grey solid

#### Volatility and van der Waals

**Fluorine** has the lowest melting and boiling points in group 7 and is therefore the **most volatile**. This is because it has the **weakest van der Waals** (intermolecular) forces.

The number of electrons in each molecule and the size of the molecules increases down group 7. This means that the **temporary dipoles** get stronger so there are more **van der Waals forces** between molecules. More energy is needed to overcome these forces so **volatility decreases** down Group 17.

### Bond Strengths of Halogen Molecules

The covalent bonds are weaker moving down the group because the halogen atoms get larger, their atomic radius increases. This means that the **bonding pair gets further away from the nucleus** and shielding increases so the attraction gets **weaker**. This means the bonds get easier to break.

## Chemical Properties of the Elements and their Hydrides

### Reactivity of the Elements as Oxidising Agents

When the halogens react, they **gain an electron** to form negative ions. **Reactivity** of the halogen **decreases** down the group. This is because it becomes harder to gain an electron as **electron shielding** and **atomic radius** increase down the group so there is weaker attraction between the incoming electron and the protons in the nucleus.

**Oxidising agents** are elements/compounds that gain electrons to oxidise another element/compound. Halogens act as oxidising agents and they become **less oxidising down the group** due to the decreasing reactivity. The relative oxidising strengths of the halogens can be seen by their **displacement** reactions with other halide ions.

The table below shows that out of chlorine, bromine and iodine, **chlorine** is the **strongest oxidising agent** and iodine is the weakest:



Halogen	Displacement	Ionic equation
Cl	Chlorine (Cl <sub>2</sub> ) will displace bromide and iodide ions.	$\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$ $\text{Cl}_2 + 2\text{I}^- \rightarrow 2\text{Cl}^- + \text{I}_2$
Br	Bromine (Br <sub>2</sub> ) will displace iodide ions.	$\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$
I	Iodine (I <sub>2</sub> ) will not react with chloride or bromide ions	No reactions take place

From this table, you can observe the **basic trend**:

*'A halogen will displace a halide from a solution if the halide ion is below it in the periodic table.'*

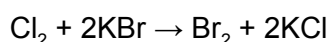
**Displacement** reactions can be identified by a **change in the colour** of the solution.

Chlorine solution - **colourless**

Bromine solution - **orange**

Iodine solution - **brown**

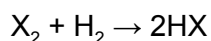
For example, if chlorine is added to a solution of potassium bromide, the solution will change from colourless to orange due to the formation of bromine:



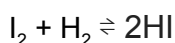
### Reaction with Hydrogen

The halogens react with hydrogen to form **hydrogen halides**. These reactions show that **reactivity decreases** down Group 17.

The standard reaction equation for the reaction with hydrogen (where X is the halogen) is:



- **Fluorine** reacts **explosively** with hydrogen to form hydrogen fluoride gas. This reaction occurs even in a **cold** atmosphere.
- **Chlorine** reacts with hydrogen if **lightly heated** or exposed to **sunlight**.
- **Bromine** reacts with hydrogen if **heated** with a flame.
- **Iodine** only partially reacts with hydrogen when **constantly heated**. There is a **partial reaction** because an **equilibrium** is set up:



## Thermal Stability of the Hydrides

The **thermal stability** of a hydride is how easy a hydrogen halide is broken up into its constituent elements when heated.

- **Hydrogen fluoride** and **hydrogen chloride** are **very thermally stable**. They will not split into hydrogen and the halogen if heated under laboratory conditions.
- **Hydrogen bromide** will **split** into hydrogen and bromine when **heated**.
- **Hydrogen iodide** will split into hydrogen and iodine **more easily than hydrogen bromide**.

These reactions show that **thermal stability of the hydrides decreases down Group 17**. This is because further down the group, the **covalent bonds are weaker** so they can be broken more easily upon heating. The bonds are weaker further down the group because the halogen atoms get larger. This means that the **bonding pair gets further away from the nucleus** so the attraction gets **weaker** and the bond is easier to break.

## Bond Energies

### Bond enthalpies of the hydrides

The thermal stability of the halogens decreases down the group. This can be explained in terms of bond energies (also known as bond enthalpies). Bond enthalpies of the hydrogen halides **decrease** down Group 17 because the size of the halogen **increases**. This means less energy is required to break the covalent bond between hydrogen and halogen.

### Bond enthalpies of the halogens

The **bond enthalpies** of the halogen molecules **decrease** from  $\text{Cl}_2$  to  $\text{I}_2$ . This is because the size of the molecules **increases** so the bonding pair is further from the nucleus. In the same way as the hydrogen halides, the **bonding pair is less attracted** to the nucleus in larger molecules so the covalent bond is more easily broken.

## Reactions of the Halide Ions

### Reactions of Halide Ions as Reducing Agents

When the halide ions react, they **lose an electron**. **Reactivity** of the halide ions **increases** down the group. This is because it becomes easier to lose an electron as **electron shielding** and **atomic radius** increase down the group so there is weaker attraction between the outer electrons and the protons in the nucleus.

**Reducing agents** are elements/ compounds that lose electrons to reduce another element/ compound. Halide ions act as reducing agents and they become **more reducing down the group** due to the increasing reactivity.

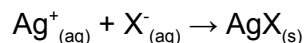


## Reactions with Silver Nitrate followed by Aqueous Ammonia

**Silver nitrate solution** can be used to **test for halide ions** in a solution:

1. Add **nitric acid** to the halide ion solution to remove any ions which may produce a false positive for the test (e.g. carbonate ions).
2. Add a few drops of **silver nitrate** solution ( $\text{AgNO}_3$ ).
3. Observe the **precipitate** formed.

The standard equation for this reaction (where X is the halide ion) is:



*Observations:*

- **Fluoride** ions - no precipitate.
- **Chloride** ions - white precipitate.
- **Bromide** ions - cream precipitate.
- **Iodide** ions - yellow precipitate.

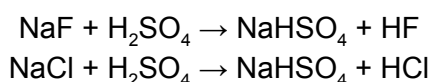
To ensure the precipitates have been correctly identified, **aqueous ammonia** can be added:

- **Chloride precipitate** - soluble in dilute  $\text{NH}_3$ .
- **Bromide precipitate** - soluble in concentrated  $\text{NH}_3$ .
- **Iodide precipitate** - insoluble in dilute and concentrated  $\text{NH}_3$ .

## Reactions with Concentrated Sulfuric Acid

All halide ions react with **concentrated sulfuric acid** to produce a **hydrogen halide**. A secondary reaction then takes place, which differs depending on which halide.

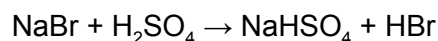
Reaction of **NaCl** and **NaF** with  $\text{H}_2\text{SO}_4$



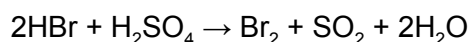
For both of these reactions, HF and HCl can be identified as **misty fumes**.

HF and HCl are **not strong enough reducing agents** so no further reactions occur.

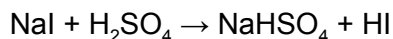
Reaction of **NaBr** with  $\text{H}_2\text{SO}_4$



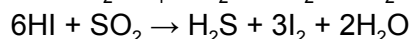
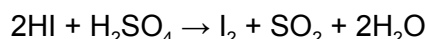
**Misty fumes** of HBr are produced. HBr is a strong enough **reducing agent** to react with  $\text{H}_2\text{SO}_4$ . This second reaction produced the **choking gas  $\text{SO}_2$**  and **brown fumes of  $\text{Br}_2$**  in a **redox reaction**:



### Reaction of **NaI** with $\text{H}_2\text{SO}_4$



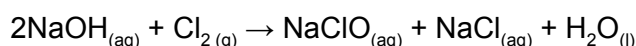
**Misty fumes** of HI are produced. HI is a strong enough **reducing agent** to react with the  $\text{H}_2\text{SO}_4$ . Similarly to the reaction above,  **$\text{SO}_2$**  is produced. Since HI is a **very strong reducing agent**, the  $\text{SO}_2$  is further reduced to  **$\text{H}_2\text{S}$**  - which smells of **rotten eggs**.



## Reactions of Chlorine with Aqueous Sodium Hydroxide

A **disproportionation** reaction is a reaction in which an element is both **oxidised** and **reduced**.

Chlorine reacts with **cold dilute** sodium hydroxide:



This is a **disproportionation** reaction because chlorine has been **reduced** from 0 in  $\text{Cl}_2$  to -1 in NaCl and **oxidised** from 0 in  $\text{Cl}_2$  to +1 in NaClO. NaClO (also known as **sodium chlorate(I)** solution) is **bleach**. It is used in water treatment, to bleach textiles and paper, and for cleaning because it **kills bacteria**.

Chlorine also reacts with **hot concentrated** sodium hydroxide:



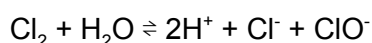
This is a **disproportionation** reaction because chlorine has been **reduced** from 0 in  $\text{Cl}_2$  to -1 in NaCl and **oxidised** from 0 in  $\text{Cl}_2$  to +5 in  $\text{NaClO}_3$ .

## Uses of Halogens and Halogen Compounds

### Chlorine in Water Purification

Chlorine is used in water purification because it **kills bacteria**.

Chlorine reacts with water in a **disproportionation** reaction, producing chloride and chlorate ions. The reaction produces HCl so an **alkali** is usually added to the water to **reduce the acidity**.



**Chlorate ions kill bacteria** so treating water with chlorine or chlorate ions makes it safe to drink or swim in.



Chlorine treats water in different ways:

- **Kills dangerous microorganisms** which could cause diseases.
- Some chlorine persists in the water which **prevents reinfection** in the long term.
- Prevents the growth of **algae**.
- **Removes bad tastes** and smells.
- Removes **discolouration**.

Chlorine is **toxic** so there are **discussions** about whether chlorine should be added to water. In addition to this, chlorine can react with organic matter in the water forming potentially **cancer** causing compounds. On balance, since only a small amount of chlorine is added, it is agreed that the **benefits outweigh the risks**.

