

GROUP VII - The Halogens

General

- non-metals
- exist as separate diatomic molecules.
- all have the electronic configuration ... $ns^2 np^5$.

TRENDS

Appearance

	F	Cl	Br	I
Colour	yellow	green	red-brown	grey
State (at RTP)	gas	gas	liquid	solid

Boiling Point

Increases down group	F	Cl	Br	I
Boiling point / °C	-188	-34	58	183

- increased size makes the van der Waals forces increase
- more energy is required to separate the **molecules**

Electronegativity

Decreases down group	F	Cl	Br	I
Electronegativity	4.0	3.0	2.8	2.5

- the increasing nuclear charge due to the greater number of protons should attract electrons more, but there is an ...
- increasing number of shells; ∴ **more shielding and less pull on electrons**
- increasing atomic radius; ∴ **attraction drops off as distance increases**

Atomic size

Increases down group	F	Cl	Br	I
Covalent radius / nm	0.064	0.099	0.111	0.128

Ionic size

Increases down group	F ⁻	Cl ⁻	Br ⁻	I ⁻
Ionic radius / nm	0.136	0.181	0.195	0.216

- **The greater the atomic number the more electrons there are.**
These go into shells increasingly further from the nucleus.
- **Ions are larger than atoms** - extra repulsion due to added electron expands radius

Oxidising power

- halogens are oxidising agents - they **need an electron to complete their octet**
- the oxidising power **gets weaker down the group**
- the trend can be explained by considering the nucleus's attraction for the incoming electron which is affected by the...
 - increasing nuclear charge which should attract electrons more; **but this is offset by**
 - increasing shielding
 - increasing atomic radius

This can be demonstrated by reacting the halogens with other halide ions.

chlorine oxidises bromide ions to bromine $\text{Cl}_2 + 2\text{Br}^- \longrightarrow \text{Br}_2 + 2\text{Cl}^-$

chlorine oxidises iodide ions to iodine $\text{Cl}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Cl}^-$

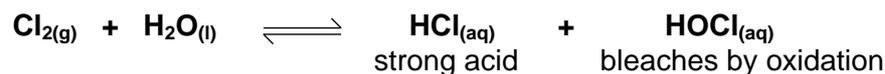
bromine oxidises iodide ions to iodine $\text{Br}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Br}^-$

As a result of its **small size** and **high electronegativity**, fluorine can bring out the highest oxidation state in elements
e.g. PF_5 (+5), SF_6 (+6), IF_7 (+7) and F_2O (+2).

Some reactions of chlorine*Water*

Halogens react with decreasing vigour down the group as their oxidising power decreases

Litmus will be turned **red** then **decolourised** in chlorine water



Q.1 What happens to the oxidation state of chlorine in this reaction?

Q.2 Explain the colour changes of litmus.

Alkalis

Chlorine reacts with aqueous sodium hydroxide. The products vary with conditions.



Q.3 What is the industrial importance of this reaction ?

HALIDE IONS**Reducing ability**

- halide ions behave as reducing agents
- they give an electron to the substance they are reducing $\text{Cl}^- \longrightarrow \text{Cl} + \text{e}^-$

Trend *least powerful* $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ *most powerful reducing agent*

Reason As the radius of the ions get larger it becomes easier to remove the outer electrons.

HYDROGEN HALIDES

Boiling points At room temp. and pressure HCl, HBr, HI are colourless gases, HF a colourless liquid.

boiling points ... **HF 20°C** **HCl -85°C** **HBr -69°C** **HI -35°C**

The HF value is much higher than expected due to **hydrogen bonding**

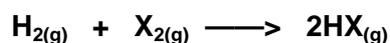
Reducing ability

- **Increases down the group** as the bond strength decreases

bond energy / kJ mol⁻¹ **H-F 568** **H-Cl 432** **H-Br 366** **H-I 298**

Preparation*Direct**combination*

Hydrogen halides can be made by direct combination



- conditions*
- fluorine is explosive even in the dark
 - chlorine combines explosively when heated or in sunlight
 - bromine is fast at 200°C with a catalyst
 - iodine reaction is reversible.

Displacement Chlorides are made by displacing the acid from its salt



HBr and HI are not made this way because they are more powerful reducing agents and are oxidised by the sulphuric acid to the halogen



TESTING FOR HALIDES - Summary

- Silver nitrate*
- make a solution of the halide
 - acidify with dilute nitric acid to prevent the formation of other insoluble silver salts
 - add a few drops of silver nitrate solution
 - treat any precipitate with dilute ammonia solution
 - if a precipitate still exists, add concentrated ammonia solution

CHLORIDE	white ppt of AgCl	soluble in dilute ammonia
BROMIDE	cream ppt of AgBr	insoluble in dilute ammonia but soluble in conc.
IODIDE	yellow ppt of AgI	insoluble in dilute and conc. ammonia solution.

the halides are precipitated as follows $\text{Ag}^+_{(\text{aq})} + \text{X}^-_{(\text{aq})} \longrightarrow \text{Ag}^+\text{X}^-_{(\text{s})}$

when they dissolve in ammonia the diammine complex is formed $[\text{Ag}(\text{NH}_3)_2]^+_{(\text{aq})}$

Q.4 What use is made of silver salts ?

- Conc. H₂SO₄*
- add concentrated sulphuric acid carefully to a **solid halide**
 - sulphuric acid displaces the weaker acids HCl, HBr, and HI from their salts
 - hydrogen halides all fume in moist air
 - as they **become more powerful reducing agents down the group** they can react further by reducing the sulphuric acid to lower oxidation states of sulphur.

Summary

Halide	Observation(s)	Product	O.S.	Reaction type
NaCl	misty fumes	HCl	-1	Displacement of Cl ⁻
NaBr	misty fumes	HBr	-1	Displacement of Br ⁻
	brown vapour	Br ₂	0	Oxidation of Br ⁻
	colourless gas	SO ₂	+4	Reduction of H ₂ SO ₄
NaI	misty fumes	HI	-1	Displacement of Cl ⁻
	purple vapour	I ₂	0	Oxidation of I ⁻
	colourless gas	SO ₂	+4	Reduction of H ₂ SO ₄
	yellow solid	S	0	Reduction of H ₂ SO ₄
	bad egg smell	H ₂ S	-2	Reduction of H ₂ SO ₄

Volumetric analysis of chlorate(I) solutions

Basic Chlorate(I) ions are oxidising agents. In acid solution they end up as chloride ions



Analysis 1 Add excess potassium iodide; the chlorate oxidises the iodide ions to iodine



$$\text{moles of I}_2 \text{ produced} = \text{original moles of OCl}^- \quad \text{----- (i)}$$

2 Titrate the iodine produced with a standard solution of sodium thiosulphate using starch as the indicator near the end point



$$\text{moles of I}_2 = \frac{1}{2} \times \text{moles of S}_2\text{O}_3^{2-} \quad \text{----- (ii)}$$

$$\text{from (i) and (ii)} \quad \text{original moles of OCl}^- = \frac{1}{2} \times \text{moles of S}_2\text{O}_3^{2-}$$

Example 25cm³ of diluted bleach solution was treated with excess potassium iodide. The iodine liberated reacted with 24 cm³ of 0.1M sodium thiosulphate solution using starch indicator at the end point. Calculate the concentration (in mol dm⁻³) of ClO⁻ in the bleach solution.

$$\begin{aligned} \text{moles of S}_2\text{O}_3^{2-} &= 0.1 \times 24/1000 &= 2.4 \times 10^{-3} \\ \text{moles of OCl}^- \text{ in } 25\text{cm}^3 &= \frac{1}{2} \times \text{moles of S}_2\text{O}_3^{2-} &= 1.2 \times 10^{-3} \\ \text{moles of OCl}^- \text{ in } 1000\text{cm}^3 &= 40 \times \text{moles of OCl}^- \text{ in } 25 \text{ cm}^3 &= 4.8 \times 10^{-2} \end{aligned}$$

$$\text{ANS.} \quad \text{Concentration of OCl}^- = 0.048\text{M}$$

Q.5 To find the amount of chlorine in a 500cm³ bottle of BIGBLEACH, a student pipetted 10cm³ out and made it up to 100cm³ with distilled water. A 25cm³ portion of this new solution was treated with excess KI. The resulting iodine reacted with 30cm³ of 0.200M Na₂S₂O₃. Calculate the mass of chlorine (Cl₂) in the original bottle of BIGBLEACH.