THE HALOGENS - Group 17 (7)

General

- non-metals
- exist as separate diatomic molecules.
- all have the electronic configuration **...** $n\mathbf{s}^2$ $n\mathbf{p}^5$.

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 induced diploe-dipole (V de W) interactions 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**

- 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** - 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 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 $Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$

chlorine oxidises iodide ions to iodine $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$

bromine oxidises iodide ions to iodine $Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$

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

Halogen reactivity with decreases down the group as oxidising power decreases
Litmus will be turned **red** then **decolourised** in chlorine water

$$Cl_2(g) + H_2O(l) \rightleftharpoons \underset{\text{strong acid}}{HCl(aq)} + \underset{\text{bleaches by oxidation}}{HOCl(aq)}$$

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

Q.2 *Explain the colour changes of litmus.*

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

Alkalis

Chlorine reacts with aqueous sodium hydroxide; the products vary with conditions.

cold, dilute $2NaOH(aq) + Cl_2(g) \longrightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$

HALIDE IONS

Reducing ability

- halide ions behave as reducing agents
- they give an electron to what they are reducing $Cl^- \longrightarrow Cl + e^-$

Trend *least powerful* $F^- < Cl^- < Br^- < I^-$ *most powerful reducing agent*

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

Example The reaction between solid halides and **concentrated sulphuric acid** - *see below*

TESTING FOR HALIDE IONS

Silver nitrate

- make a solution of the halide
- acidify with **dilute nitric acid** - prevents 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

Halide ion	*Precipitate*	*Colour*	*Solubility in dilute ammonia solution*	*Solubility in conc. ammonia solution*
Chloride	AgCl	WHITE	SOLUBLE	SOLUBLE
Bromide	AgBr	CREAM	INSOLUBLE	SOLUBLE
Iodide	AgI	YELLOW	INSOLUBLE	INSOLUBLE

- the halides are precipitated as follows $Ag^+(aq) + X^-(aq) \longrightarrow Ag^+X^-(s)$
- dissolving in ammonia gives the colourless diammine complex $[Ag(NH_3)_2]^+(aq)$

Q.4 *What use is made of silver salts ?*

Alternative test for halides

Add concentrated sulphuric acid carefully to a **solid halide**

Conc H_2SO_4

- 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_2SO_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_2SO_4
	yellow solid	S	0	Reduction of H_2SO_4
	bad egg smell	H_2S	-2	Reduction of H_2SO_4

AQA

HYDROGEN HALIDES

Boiling points

At room temperature and pressure HC*l*, HBr, HI — colourless gases; HF — colourless liquid

boiling points ... **HF** 20°C **HC*l*** -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**	**H-C*l***	**H-Br**	**H-I**
	568	432	366	298

Preparation

Displacement Chlorides are made by displacing the acid from its salt

$NaCl_{(s)}$ + conc. $H_2SO_{4(l)}$ ——> $NaHSO_{4(s)}$ + $HCl_{(g)}$

Direct combination Hydrogen halides can be made by direct combination

$H_{2(g)}$ + $X_{2(g)}$ ——> $2HX_{(g)}$

USES OF HALOGENS AND HALIDES

Chlorine, Cl_2
- water purification - kills bacteria (toxic / chlorinated hydrocarbon formation)
- bleach
- solvents
- polymers - poly(chloroethene) or PVC
- CFC's

Fluorine, F_2
- CFC's
- polymers - PTFE poly(tetrafluoroethene) as used in... non-stick frying pans, electrical insulation, waterproof clothing

Fluoride, F^-
- helps prevent tooth decay - tin fluoride is added to toothpaste
  - sodium fluoride is added to water supplies

Hydrogen fluoride, HF
- used to etch glass

Silver bromide, AgBr
- used in photographic film

Q.4 *The automatic addition of fluoride to public drinking water has always been controversial. Many people think it is a good thing as its use is linked to fewer fillings in children's teeth. However, it can cause permanent discolouration of teeth and liver damage.*

Some people feel that taking fluoride should be a personal choice. What are your thoughts?

Q.5
- *Why are some environmental campaigners demanding that chlorine is no longer used for purifying drinking water?*
- *Drinking bottled water bad for the environment - explain.*
- *Tap water or bottled water - which do you prefer?*