GROUP VII - The Halogens

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

TRENDS

Appearance

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

Boiling Point **Increases down group**

	F	C*l*	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	C*l*	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	C*l*	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

$$Cl_2(g) + H_2O(l) \rightleftharpoons HCl(aq) + HOCl(aq)$$

HCl(aq): strong acid; HOCl(aq): bleaches by oxidation

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

USES OF HALOGENS AND HALIDES

Chlorine, Cl_2
- water purification
- 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?*

HALIDE IONS

Reducing ability
- halide ions behave as reducing agents
- they give an electron to what they are reducing **Cl^- ——> 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.

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) **——> Ag^+X^-**(s)

dissolving in ammonia gives the colourless diammine complex **$[Ag(NH_3)_2]^+$**(aq)

Q.6 *What use is made of silver salts ?*