

GROUP VII - The Halogens

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

TRENDS

<i>Appearance</i>		F	Cl	Br	I
<i>Colour</i>		yellow	green	red-brown	grey
<i>State (at RTP)</i>		gas	gas	liquid	solid

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

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

<i>Electronegativity</i>	Decreases down group	F	Cl	Br	I
<i>Electronegativity</i>		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**

<i>Atomic size</i>	Increases down group	F	Cl	Br	I
<i>Covalent radius / nm</i>		0.064	0.099	0.111	0.128

<i>Ionic size</i>	Increases down group	F⁻	Cl⁻	Br⁻	I⁻
<i>Ionic radius / nm</i>		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 $\text{Cl}_2 + 2\text{Br}^- \longrightarrow \text{Br}_2 + 2\text{Cl}^-$

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

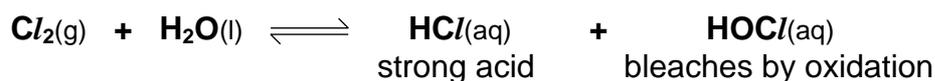
bromine oxidises iodide ions to iodine $\text{Br}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Br}^-$

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

Halogen reactivity with decreases down the group as 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.

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

Alkalis

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



USES OF HALOGENS AND HALIDES

- Chlorine, Cl₂*
- water purification
 - bleach
 - solvents
 - polymers - poly(chloroethene) or PVC
 - CFC's

- Fluorine, F₂*
- 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 $\text{Cl}^- \longrightarrow \text{Cl} + \text{e}^-$

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

Reason As the 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

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

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

dissolving in ammonia gives the colourless diammine complex $[\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$

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