Group VII - *The Halogens*

The elements of Group VII, the Halogens, are:

	symbol	electron configuration
fluorine	F	$[He]2s^2 2p^5$
chlorine	Cl	$[Ne]3s^2 3p^5$
bromine	Br	$[Ar]3d^{10} 4s^2 4p^5$
iodine	I	$[Kr]4d^{10} 5s^2 5p^5$
astatine	As	$[Xe]4f^{14} 5d^{10} 6s^2 6p^5$

All the isotopes of astatine are radioactive, and so this element will not be considered further here.

Appearance

Fluorine is a poisonous pale yellow gas, chlorine is a poisonous pale green gas, bromine is a toxic and caustic brown volatile liquid, and iodine is a shiny black solid which easily sublimes to form a violet vapour on heating.

General Reactivity

The elements of Group VII, the Halogens, are a very similar set of non-metals. They all exist as diatomic molecules, X_2, and oxidise metals to form halides. The halogen oxides are acidic, and the hydrides are covalent. Fluorine is the most electronegative element of all. Generally, electronegativity and oxidising ability decrease on descending the Group. The result of this decreasing electronegativity is increased covalent character in the compounds, so that AlF_3 is ionic whereas $AlCl_3$ is covalent.

Fluorine shows some anomalies because of the small size of its atom and ion. This allows several F atoms to pack around a different central atom, as in AlF_6^{3-} compared with $AlCl_4^-$. The F-F bond is also unexpectedly weak because the small size of the F atom brings the lone pairs closer together than in other halogens, and repulsion weakens the bond.

Occurrence and Extraction

The halogens are too reactive to occur free in nature. Fluorine is mined as fluorspar, calcium fluoride and cryolite. It is extracted by electrolysis as no oxidant will oxidise fluorides to fluorine. Chlorine is also found in minerals such as rock-salt, and huge quantities of chloride ions occur in seawater, inland lakes and subterranean brine wells. It is obtained by the electrolysis of molten sodium chloride or brine. Bromine is also found as the bromide ion in seawater, and in larger quantities in brine wells, from which it is extracted. Iodine is mined as sodium iodate(V), $NaIO_3$, which is present in Chile saltpetre. It is obtained by reaction with sodium hydrogensulphite.

Physical Properties

At room temperature all the halogens exist as diatomic molecules. The melting points, boiling points, atomic radii and ionic radii all increase on descending the Group. The shapes of the covalent molecules and ions are readily explained by VSEPR (valence shell electron pair repulsion) theory and these compounds are often used to illustrate the theory. Fluorine is never surrounded by more than 8 electrons, whereas the other halogens may be surrounded by up to 14 electrons.

Chemical Properties

The most characteristic chemical feature of the halogens is their ability to oxidise. Fluorine has the strongest oxidising ability, so other elements which combine with fluorine have their highest possible oxidation number. Fluorine is such a strong oxidising agent that it must be prepared by electrolysis. Chlorine is the next strongest oxidising agent, but it can be prepared by chemical oxidation. Most elements react directly with chlorine, bromine and iodine, with decreasing reactivity going down the Group, but often the reaction must be activated by heat or UV light. The oxidation of thiosulphate ions, $S_2O_3^{2-}$, by the halogens is quantitative. This means that oxidising agents can be estimated accurately; the oxidising agent is reacted with excess I^- ions, and the liberated I_2 titrated with standard thiosulphate solution. The end point is detected with starch as indicator, which forms a dark blue complex with iodine. Chlorine, bromine and iodine disproportionate in the presence of water and alkalis.

Oxides and Oxoacids

There are no fluorine oxides as F is more electronegative than O. Chlorine, bromine and iodine each form several oxides which are thermally unstable, such as chlorine dioxide ClO_2. The only fluorine oxoacid, HOF, is unstable at room temperature, but there are many oxoacids of the other halogens. The best known salts of these are; hypochlorite, chlorate(I) ClO^-, chlorite, chlorate(III) ClO_2^-, hypochlorate, chlorate(V) ClO_3^-, perchlorate, chlorate(VII) ClO_4^- . These are all powerful oxidising agents.

Halides

The halogens can combine with each other to form interhalogens and polyhalide ions.

Polyhalide ions have the general formula $[Y\text{-}X\text{-}Y]^-$. It is not possible for F to represent X in a polyhalide ion as it cannot expand its octet.

Hydrides

Hydrogen halides have the general formula HX. HF is a colourless liquid which boils at 19.5°C, and all the other hydrogen halides are colourless gases. HF is a liquid due to the extensive hydrogen bonding which occurs between molecules. All the hydrogen halides dissolve easily to give acidic solutions, the most widely used being hydrochloric acid, HCl. All except HF are typical acids; they liberate carbon dioxide from carbonates and form salts with basic oxides. HF is a weak acid because the H-F bond is very strong, and because hydrogen-bonding occurs between F^- and HF in solution.

Organic Compounds

The halogens form organic compounds which are best known for their industrial and environmental impact, such as PVC, DDT and TCP.

Oxidation States and Electron Affinities

Fluorine in all its compounds has an assigned oxidation number of -1, as it is the most electronegative of all the elements. The other halogens show a wide range of oxidation numbers, and the redox chemistry of these halogens is important. The oxidation numbers most commonly shown are odd; there are few compounds with even oxidation numbers and they are often thermally unstable. Chlorine is the 3rd most electronegative element after F and O. The halide ions are readily formed by accepting 1 electron, as this completes an octet of valence electrons. The electron affinity decreases on descending the Group.

Industrial information

The halogens are probably the most important Group of the Periodic Table used in industry. Fluorine is widely used as an oxidising agent. HF is used to etch glass. Chlorine is used for chlorinating drinking water, and in many organochlorine compounds. Some of these, such as the insecticide DDT, are effective but environmentally damaging, and much controversy surrounds their use. Chlorine dioxide is used to bleach wood pulp for paper making, as it gives a good whiteness without degrading the paper. Hypochlontes are used in domestic bleaches. Potassium chlorate (V) is used as an oxidant in fireworks and matches. Ammonium chlorate (VII) is used as a fuel in space rockets when mixed with powered aluminium.

Further Information

For further information look up the individual elements.

Data

	Atomic Number	Relative Atomic Mass	Boiling Point/K	Density/kg m^{-3}
F	9	19.99	885.01	1.696
Cl	17	35.45	3239.18	3.214
Br	35	79.90	4331.93	7.59 (gas)
I	53	126.90	4457.50	4930

Electron Affinity (M-M^-)kJ mol^{-1}

F	333
Cl	348
Br	324
I	295

Ionisation Energies/kJ mol^{-1}

	1st	2nd	3rd	4th
F	1681	3374	6050	8408
Cl	1251.1	2297	3826	5158
Br	1139.9	2104	3500	4560
I	1008.4	1845.9	3200	4100

	5th	6th	7th	8th
F	11023	15764	17867	92036
Cl	6540	9362	11020	33610
Br	5760	8550	9940	18600
I	5000	7400	8700	16400

	Atomic Radius/nm	Covalent Radius/nm	Ionic Radius/nm (X^-)
F	0.0709	0.064	0.133
Cl	0.0994	0.099	0.181
Br	0.1145	0.1142	0.196
I	0.1331	0.1333	0.220