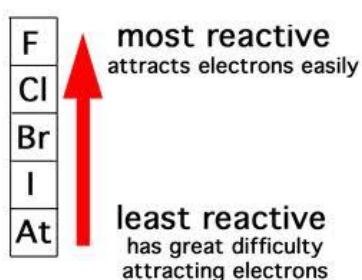




Group 7 Elements

P.J.McCormack



Oxidised
Low Boiling Point
Volatile
Astatine
Iodine
Covalent Bonding
F₂
Diatomic
Nuclear Attraction
Van Der Waals Forces
Reactive Chlorine
Reduced Redox
Group 7
Shielding
Water Purification
Disproportionation
Low Melting Point
I₂
Oxidising Agent
Water Treatment
Fluorine
Cl₂ Halogen
Silver Nitrate
Ammonia
Bleach
Br₂ At₂
Toxic
Bromine
Halide

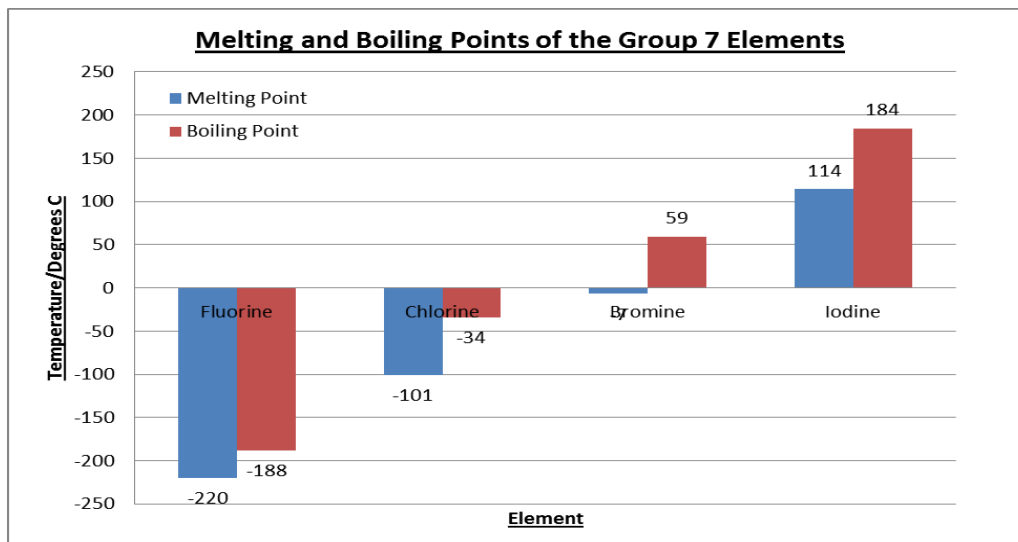
Introduction

- (a) Fluorine, chlorine, bromine and iodine belong to a family of elements called the halogens ('salt producing'). All four elements are very reactive non-metals. They are not found free in nature but exist as compounds with metals.
- (b) A halide is a halogen atom with a -1 charge e.g. Cl^- , Br^- , I^- .
- (c) The halogens are important economically as the ingredients of plastics, pharmaceuticals, photographic chemicals, anaesthetics and dyestuffs.
- (d) They all consist of diatomic molecules, X_2 , which are linked by a single covalent bond. They are **volatile**. The intermolecular (van der Waal's) forces increase down the group as the number of electrons in the atoms increase.
- (e) They are strong oxidising agents so are able to gain one electron easily.
- (f) At room temperature,
- Fluorine is a pale yellow gas
 - Chlorine is a yellow-green gas
 - Bromine is a dark red liquid
 - Iodine is a shiny grey/black solid
- (g) The physical properties of the halogens are as follows:

| Halogen | Electron configuration | Atomic radius /nm | Ionic radius /nm | Melting point / $^{\circ}\text{C}$ | Boiling point / $^{\circ}\text{C}$ | Electro-negativity | Electron affinity kJ mol ⁻¹ |
|----------|---------------------------------|-------------------|------------------|------------------------------------|------------------------------------|--------------------|--|
| Fluorine | $1s^2 2s^2 2p^5$ | 0.071 | 0.133 | -220 | -188 | 4.0 | 333 |
| Chlorine | $1s^2 2s^2 2p^6 3s^2 3p^5$ | 0.099 | 0.180 | -101 | -34 | 3.0 | 348 |
| Bromine | $[\text{Ar}] 3d^{10} 4s^2 4p^5$ | 0.114 | 0.195 | -7 | 58 | 2.8 | 340 |
| Iodine | $[\text{Kr}] 4d^{10} 5s^2 5p^5$ | 0.133 | 0.215 | 114 | 184 | 2.5 | 297 |
| Astatine | $[\text{Xe}] 5d^{10} 6s^2 6p^5$ | 0.140 | - | ? | | - | - |

I.3.1 (a) Trend in Boiling Point

- (a) It can be seen from the graph below that the boiling point of the halogens increases steadily down the group. This is accounted for by the differences in strength of the intermolecular forces – the **van der Waal's** forces.



- (b) Van der Waal's forces are attractive (electrostatic) forces that act between molecules because of **the uneven distribution of electrons** in the molecules.
- (c) The electron distribution changes from one instant to the next. Each time it changes a temporary dipole (difference in charge) is produced with one end of the molecule more negative and the other less negative. This **induces** an adjacent molecule to become a temporary dipole as well. The attraction between the oppositely charged ends holds the molecules together:

An instant:



Temporary dipole

There are more electrons on the right of the molecule, so the right has a small negative charge, causing a small δ^-



Induced dipole

The negative charge of the **temporary dipole** repels the electrons to the other side of the molecule, producing an induced dipole positive charge on the left.

- (d) The boiling point of fluorine is -188°C . The dipoles formed by its few electrons do not produce sufficiently strong intermolecular van der Waal's forces for it to be a liquid at room temperature. Chlorine has more electrons and produces stronger dipoles and a greater intermolecular attraction, so its boiling point is higher, -35°C .
- (e) The larger molecules of bromine and iodine have more electrons and successively greater van der Waal's forces.
- (f) Thus the **volatility** – the tendency to become gaseous – decreases down Group VII.

1.3.3 (b) Redox Reactions

- (a) **An oxidising agent is a substance that will accept electrons. The ability of the halogens to accept an electron to form a halide ion makes them very good oxidising agents.**



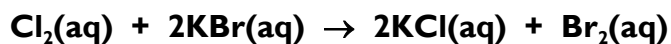
- (b) The oxidising power decrease down the group i.e. $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

| Halogen | Halogen Water Colour | Halogen Colour in Cyclohexane |
|---------------|----------------------|-------------------------------|
| Cl_2 | Pale-green | Pale-green |
| Br_2 | Orange | Orange |
| I_2 | Brown | Violet |

- (c) Redox reactions can show that halogens become less able to form halide ions down the group. This is demonstrated by redox reactions of the halogens (Cl_2 , Br_2 , I_2) with aqueous solutions of the halides (Cl^- , Br^- , I^-). When a halogen is mixed with an aqueous solution of the halides, the more reactive halogen will displace the less reactive halide. These reactions are called **displacement reactions**.
- (d) When a pale yellowish solution of chlorine water is added to colourless potassium bromide a reddish-brown solution of bromine forms. The bromide ion is oxidized to bromine by the chlorine:

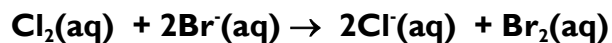


- (e) Halogen will form solutions with different colours, and any change in colour will indicate that a redox reaction has taken place. The table below shows the resulting colours when the halogen water/solution is added to a solution containing the halide ion such as potassium halides. The colour produced is caused by the least reactive halogen being produced, e.g. when chlorine (Cl_2) is added to potassium bromide solution (KBr) the chlorine will displace the Br^- in potassium bromide forming Br_2 which has a characteristic orange colour and potassium chloride.

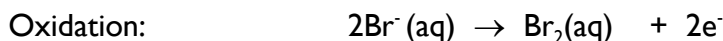


| Halogen | Halide Solution | | |
|---------------|-----------------|-----------------|----------------|
| | KCl | KBr | KI |
| Cl_2 | | Orange solution | Brown solution |
| Br_2 | No reaction | | Brown solution |
| I_2 | No reaction | No reaction | |

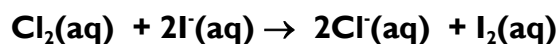
- Chlorine will oxidise both Br^- and I^- ions:



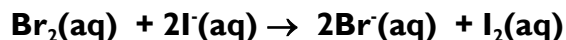
This equation can be written as half equations:



Chlorine is the stronger oxidising agent because it takes an electron from each bromide ion to produce bromine atoms which then combine to form bromine molecules. It **displaces** bromine from solution.



- Bromine will only oxidise I^- ions



1.3.3 (c) Trend in Reactivity Down Group 7

The reactivity decreases as you go down the group because:

- The atomic radius increases
- The electron shielding increases
- The nuclear attraction decreases

Exam tip: You must make sure you mention these three points when explaining the trend in reactivity.

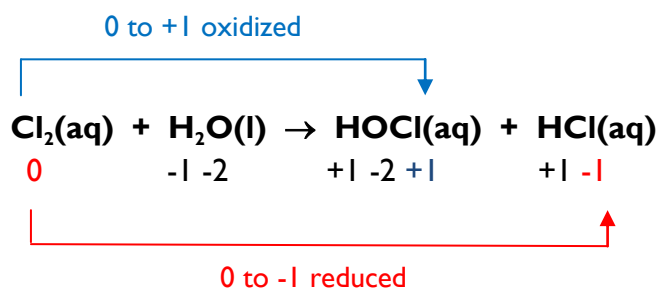
The results in a lower ability to gain an electron into the p sub-shell decreases to form a halide ion.

1.3.3 (d) Chlorine and Water Purification

- (a) Chlorine is added to drinking water to destroy any harmful bacteria and viruses. The chlorine is pumped into the water, which is then left to stand for two hours to complete the disinfection.
- (b) The chlorine reacts with the water to form an acidic solution containing hydrochloric acid and **chloric(I) acid (HOCl)**.



Exam tip: Memorize this equation it frequently appears in exam.



- (c) The reaction above is an example of **disproportionation**. Disproportionation is when the same element becomes oxidized and reduced. The uncombined chlorine on the left of the equation has an oxidation number of zero. The chlorine in chloric(I) acid has an oxidation number of **+1** ((+1) + (-2) + Cl = 0) and has been oxidized. The chlorine in hydrochloric acid has an oxidation number of **-1** which has been reduced.
- (d) Water in swimming pools is disinfected in a similar way.

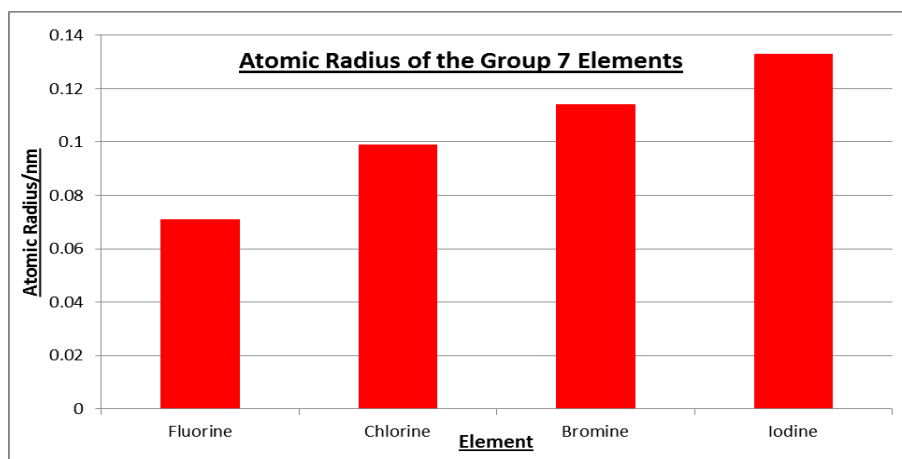
- (e) The reaction of chlorine with aqueous sodium hydroxide is another example of disproportionation. Household bleach is formed when chlorine and is added to cold **dilute sodium hydroxide** solution. The active ingredient in household bleach is sodium chlorate(I) (NaOCl).



1.3.3 (e) Trends in Physical Properties

Atomic Radius

- (a) The atomic radius increases down the group with the increasing number of electron shells.
- (b) The positive charge of the nucleus increases down the group. This pulls the electron shells closer so tending to decrease the size of the atom. However the addition of more shells more than counteracts this.
- (c) Additionally, each outer shell is shielded from the pull of the nucleus by the inner shells resulting in the increased atomic radii down the group.



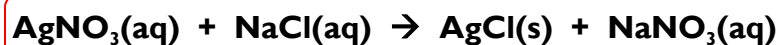
Electronegativity

- (a) **The electronegativity of an atom is a measure of the force of attraction of its nucleus for the electrons of other atoms bonded with it.**
- (b) Atoms, which attract electrons strongly, are said to be strongly electronegative and high electronegativity tends to make an element very reactive.
- (c) The electronegativity of all of the halogens is high but it decreases down the group.
- (d) Fluorine is a small atom with few shells of electrons. Consequently when it is bonded to another atom it gets close to the fluorine nucleus which is less shielded by shells of electrons. It is therefore the most electronegative of all of the elements. In hydrogen fluoride the shared electrons in the covalent bond are strongly distorted towards the fluorine atom.
- (e) Chlorine is a bigger atom and although it has more protons it also has another shell of electrons, which shields the nucleus. It is therefore not as electronegative as fluorine but still remains a very reactive element.
- (f) Similarly bromine and iodine with further shells of electrons are less electronegative.

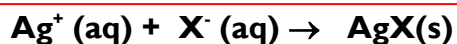
1.3.3 (f) Benefits of Using Chlorine as an Anti-Bacterial Agent in Water.

I.3.3 (g & h) Chemical Tests for Halides

- (a) Precipitation reactions with silver nitrate and ammonia can be used to identify halide ions.
- (b) Most halides are soluble in water. They can be detected in solution by adding nitric acid and then silver nitrate solution. This produces a precipitate. (The nitric acid will dissolve any metal carbonate, which also produces a precipitate with silver nitrate.)
- (c) The precipitates formed are either insoluble silver chloride, silver bromide or silver iodide. It is possible to identify the halide present from the colour of the precipitate. Silver chloride is white, silver bromide is cream and silver iodide is pale yellow.



Ionically



- (d) However it is not always easy to distinguish between the colours. To confirm the results ammonia solution is added. Silver chloride is soluble in ammonia solution and so the precipitate dissolves. Silver bromide is sparingly soluble (slightly soluble) in dilute ammonia solution but soluble in concentrated ammonia solution. Silver iodide does not dissolve in either dilute or concentrated ammonia solution (the precipitate does turn white).

| Halide Ion | Reaction with silver nitrate solution | Reaction with <u>dilute</u> aqueous ammonia | Reaction with <u>concentrated</u> aqueous ammonia |
|------------|---|---|---|
| Fluoride | No precipitate | No precipitate | No precipitate |
| Chloride | White precipitate of silver chloride. (AgCl) | Soluble | Soluble |
| Bromide | Cream precipitate of silver bromide. (AgBr) | Insoluble | Soluble |
| Iodide | Yellow precipitate of silver iodide. (AgI) | Insoluble | Insoluble |