

Topic 2.5

GROUP VII, THE HALOGENS

Introduction to the Halogens

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INTRODUCTION TO THE HALOGENS

The **halogens** are the collective name given to the elements in group VII of the Periodic Table. There are five halogens; fluorine, chlorine, bromine, iodine and astatine. Astatine is very radioactive and cannot exist for more than a few microseconds before decaying. We will thus be concerned with the chemistry of fluorine, chlorine, bromine and iodine.

All these elements are most commonly found in the -1 oxidation state, as X^- ions. These are known as **halide** ions.

i) Structure

Since each atom in this group has seven valence electrons, they tend to form diatomic molecules, eg F_2 , Cl_2 , Br_2 and I_2 . They are thus simple molecular, with weak intermolecular forces between the molecules.

ii) Appearance and colour

Halogen	In pure form	In non-polar solvents	In water
Fluorine	Pale yellow gas	- (Reacts with solvents)	- (Reacts with water)
Chlorine	Pale green gas	Pale green solution	Pale green solution
Bromine	Dark red liquid	Orange solution	Orange solution
Iodine	Grey solid	Purple solution	- (Insoluble) but forms a brown solution if excess KI is present

The halogens are usually used in aqueous solution. Although iodine is insoluble in water, it is soluble if iodide ions are present (the iodine reacts with iodide ions to form triiodide ions as follows: $I_2(aq) + I^-(aq) \rightarrow I_3^-(aq)$). The triiodide ions give the solution its brown colour.

iii) Melting and boiling points

Halogen	Melting point /°C	Boiling point /°C
Fluorine	-220	-188
Chlorine	-101	-35
Bromine	-7	59
Iodine	114	184

The melting and boiling points of the halogens increase steadily down the group. This is due to the increase in strength of the Van Der Waal's forces between the molecules, which results from the increasing number of electrons in the molecule and the increasing surface area of the molecule.

iv) Electronegativity

Electronegativity is the ability of an atom to attract electrons in a covalent bond. The electronegativity of the halogen atoms decreases down a group:

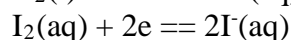
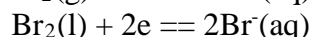
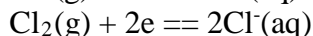
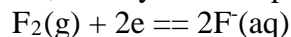
Halogen	Electronegativity
F	4.0
Cl	3.0
Br	2.8
I	2.5

As the number of shells increases, the shielding increases and the electrons in the covalent bond are further from (and more shielded from) the nucleus. Therefore they are less strongly attracted to the nucleus and the electronegativity decreases.

REDOX PROPERTIES OF HALOGENS AND HALIDE IONS

i) The halogens – oxidising agents

All the halogens are oxidising agents, as they can accept electrons and get reduced:



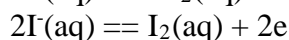
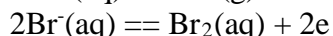
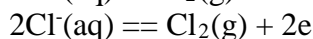
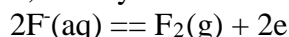
Fluorine is the best oxidising agent, followed by chlorine. Iodine is a mild oxidising agent. The fewer the number of shells in the atom, the closer the electrons can get to the nucleus and the less shielded the electrons are from the nucleus. The attraction of the electrons to the nucleus is thus stronger and the atom is more likely to accept electrons.

Thus the oxidising power of the halogens decreases down a group:

Fluorine	chlorine	bromine	iodine
Very strong oxidising agent	Strong oxidising agent	Fairly strong oxidising agent	Mild oxidising agent

ii) The halides – reducing agents

The halide ions are reducing agents, as they can lose electrons and get oxidised:



Iodide ions are the most reducing, followed by bromide ions. Fluoride ions have no significant reducing properties. As the number of shells in the ion increases, there is more shielding of the nucleus and the outer electrons become less strongly held. These electrons are thus lost more easily and the halide ion is more readily oxidised.

Thus the reducing power of the halides increases down a group:

Fluoride	chloride	bromide	iodide
Very poor reducing agent	Poor reducing agent	Fairly poor reducing agent	Fairly good reducing agent

iii) Displacement reactions between halogens and halide ions

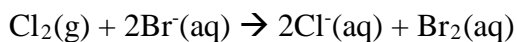
The displacement reactions of halogens with halide ions provides a clear illustration of the trends in oxidizing properties of the halogens and the trends in reducing properties of the halide ions in aqueous solution:

The more reactive halogens (ie the strongest oxidising agents) will displace the more reactive halides (ie the strongest reducing agents) from solutions of their ions:

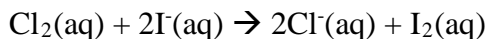
Chlorine will displace bromide and iodide ions from solution.

Bromine will displace iodide ions from solution, but not chloride ions.

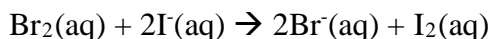
Iodine cannot displace either bromide or chloride ions from solution.



Orange colour will appear in solution on adding chlorine



Brown colour will appear in solution on adding chlorine



Brown colour will appear in solution after adding bromine

$\text{I}_2(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{Cl}_2(\text{g})$ will not happen

$\text{I}_2(\text{aq}) + 2\text{Br}^-(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{Br}_2(\text{g})$ will not happen

$\text{Br}_2(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + \text{Cl}_2(\text{g})$ will not happen

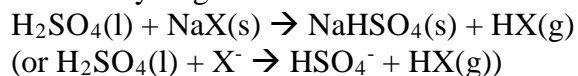
These reactions will not happen as chlorine is a stronger oxidising agent than bromine and bromine is a stronger oxidising agent than iodine.

As size increases down a group, the ability of the atoms to accept electrons decreases and hence their oxidising power decreases.

iv) Reaction of halide ions with concentrated sulphuric acid

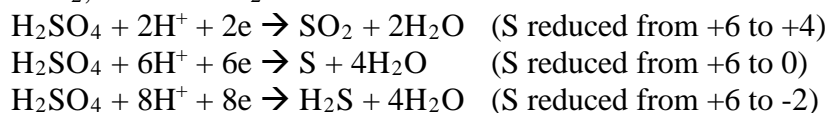
The variation in reducing strength of the halides can be clearly seen in the reaction of the sodium halides with concentrated sulphuric acid.

Concentrated sulphuric acid is a strong acid and can convert the sodium salts of the halides into the hydrogen halides:



The halide ions are not oxidised in this reaction; in fact they are behaving as bases.

Concentrated sulphuric acid is, however, also an oxidising agent; it can be reduced either to SO_2 , to S or to H_2S :

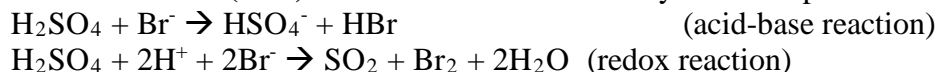


Cl⁻ is not a strong reducing agent so is not oxidised by H_2SO_4 . Only the acid-base reaction takes place and HCl gas is formed:



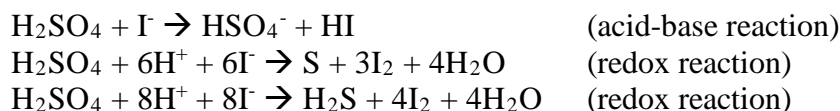
White fumes of HCl will be seen. The fumes will turn blue litmus paper red.

Br⁻ is a better reducing agent and is oxidised, but the sulphur in the H_2SO_4 is only reduced from +6 to +4 (SO_2). The acid-base reaction may also take place to an extent:



White fumes will be seen which turn blue litmus paper red. The red/orange colour of bromine will also be seen.

I⁻ is a good reducing agent and is oxidised, reducing the sulphur in the H_2SO_4 from +6 to +4 (SO_2), to 0 (S) or to -2 (H_2S). The acid-base reaction may also take place to an extent:



White fumes will be seen which turn blue litmus paper red. The purple colour of iodine vapour will also be seen and there will be a smell of rotten eggs due to the presence of H_2S .

The products of the reaction between the sodium halides and concentrated sulphuric acid can be summarized in the following table:

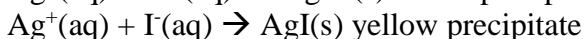
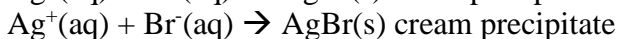
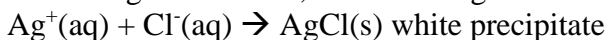
Salt	Products of reaction with concentrated sulphuric acid	Types of reaction occurring
NaCl	HCl, NaHSO ₄	Acid-base
NaBr	Br ₂ , H ₂ O, SO ₂ , NaHSO ₄	Acid-base and redox
NaI	I ₂ , H ₂ O, S, H ₂ S, NaHSO ₄	Acid-base and redox

TESTS FOR HALIDE IONS

a) reaction with silver ions

The silver (I) ion, Ag^+ , forms insoluble precipitates with the chloride, bromide and iodide ions. Each has its characteristic colour and these precipitation reactions can thus be used as chemical tests for these ions:

If **silver nitrate** solution, and a little nitric acid, is added to an aqueous solution containing a halide ion, the following reactions take place:



The **nitric acid** is added to ensure that any carbonate or hydroxide ions, often found as impurities with halide ions, are removed as CO_2 or water and so do not interfere with the precipitate.

b) Reaction of silver halides with ammonia

The three precipitates are similar in colour and thus it is not always easy to tell them apart. A further test should thus be used to distinguish between them.

If dilute or concentrated ammonia is added to $\text{AgCl}(\text{s})$, the precipitate dissolves.

If dilute ammonia is added to $\text{AgBr}(\text{s})$, there is no reaction but if concentrated ammonia is added then the precipitate dissolves.

Silver iodide does not dissolve either in dilute or in concentrated ammonia.

c) **Summary**

The full chemical tests for the three halide ions in solution can thus be summarised as follows:

- for $\text{Cl}^-(\text{aq})$: add dilute $\text{AgNO}_3(\text{aq})$, with a little nitric acid, to the solution. A white precipitate will form which is soluble in dilute ammonia.
- for $\text{Br}^-(\text{aq})$: add dilute $\text{AgNO}_3(\text{aq})$, with a little nitric acid, to the solution. A cream precipitate will form which is insoluble in dilute ammonia but soluble in concentrated ammonia.
- for $\text{I}^-(\text{aq})$: add dilute $\text{AgNO}_3(\text{aq})$, with a little nitric acid, to the solution. A yellow precipitate will form which is insoluble in dilute ammonia and also insoluble in concentrated ammonia.

Halide ion	Colour of silver halide precipitate	Solubility of precipitate in dilute NH_3	Solubility of precipitate in concentrated NH_3
Chloride	White	Soluble	Soluble
Bromide	Cream	Insoluble	Soluble
Iodide	Yellow	Insoluble	Insoluble

OTHER REACTIONS AND USES OF CHLORINE AND ITS COMPOUNDS

a) Reaction with water

Chlorine is slightly soluble in water, and actually reacts slightly with water in a disproportionation reaction:



The chlorine is simultaneously oxidised and reduced.

HClO is chloric (I) acid. It is a mild oxidising agent and effective at killing bacteria without being harmful to humans. For this reason a small amount of chlorine dissolved in water will sterilise the water and chlorine is widely used in swimming pools and in water treatment for this reason.

Chlorine is toxic to humans in anything other than very small doses, so care must be taken not to over-chlorinate the water supply.

b) Reaction with cold dilute alkali

Chlorine disproportionates readily in dilute alkali in another disproportionation reaction:



Again, the chlorine is simultaneously oxidised and reduced

The ion ClO^- is known as the chlorate (I) ion. It is an important oxidising agent and is the active ingredient in domestic bleach, NaClO.