

CHAPTER 12: Group VII

12.1 Physical Properties of Group VII Elements

12.2 Reactions of Group VII Elements

12.3 Reactions of Halide Ions

12.4 Uses of Halogens

Learning outcomes:

- (a) *describe the colours of, and the trend in volatility of chlorine, bromine and iodine.*
- (b) *interpret the volatility of the elements in terms of van der Waals' forces.*
- (c) *describe the relative reactivity of the elements as oxidising agents.*
- (d) *describe and explain the reactions of the elements with hydrogen.*
- (e) (i) *describe and explain the relative thermal stabilities of the hydrides.*
(ii) *interpret these relative stabilities in terms of bond energies.*
- (f) *describe and explain the reactions of halide ions with*
 - (i) *aqueous silver ions followed by aqueous ammonia.*
 - (ii) *concentrated sulfuric acid.*
- (g) *outline a method for the manufacture of chlorine from brine by a diaphragm cell.*
- (h) *describe and interpret in terms of changes of oxidation number the reaction of chlorine with cold, and with hot, aqueous sodium hydroxide.*
- (i) *explain the use of chlorine in water purification.*
- (j) *state the industrial importance and environmental significance of the halogens and their compounds (e.g. for bleaches, PVC, halogenated hydrocarbons as solvents, refrigerants and in aerosols).*

12.1 Physical Properties of Group VII Elements

Introduction to Group VII elements

- 1) Group VII elements(also called the '**halogens**') are p-block elements with a characteristic outer shell configuration of ns^2np^5 .

<u>Group VII elements</u>		<u>Atomic no.</u>	<u>Electronic configuration</u>
fluorine	F	9	$1s^2 2s^2 2p^5$
chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
bromine	Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
iodine	I	53	$[Kr] 4d^{10} 5s^2 5p^5$
astatine	At	85	$[Xe] 4f^{14} 5d^{10} 6s^2 6p^5$

- 2) Some common physical properties of the halogens are as follow:

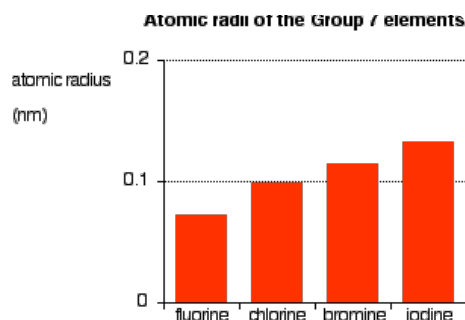
	<i>Colour and state at r.t.</i>	<i>b.p. / °C</i>	<i>Solubility</i>	
			<i>in water</i>	<i>in organic solvent</i>
F ₂	pale yellow gas	-188	–	–
Cl ₂	yellow-green gas	-35	moderately soluble	yellow solution
Br ₂	dark red liquid	58	slightly soluble	orange-brown solution
I ₂	black solid	183	insoluble	violet/purple solution

Note:

- Bromine is a dark red liquid but forms reddish-brown gas.
- Iodine is a black solid but forms a **purple vapour** on gentle heating.
- The trend is the halogens get **darker** going down the Group.
- Iodine is insoluble in water but it dissolves in potassium iodide, KI solution due to the formation of I₃⁻ ion.
- In organic solvents, halogens exist as free molecules, X₂.

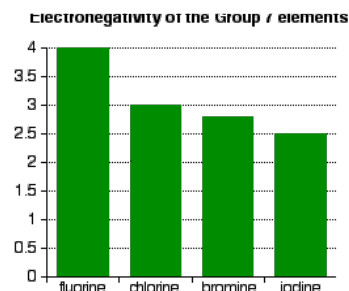
Variation in atomic radius

- 1) The atomic radius of halogens **increases** going down the Group. This is because going down the Group, each succeeding element has **one more shell of electrons**. The distance between nucleus and outer electrons are progressively further.



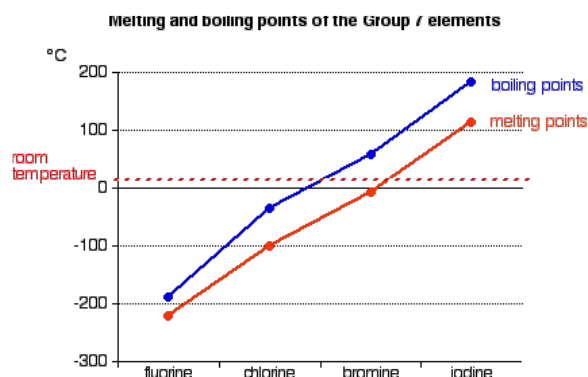
Variation in electronegativity

- 1) The electronegativity of halogens **decreases** down the Group. This is because going down the Group, the distance between the nucleus and bonding electrons increases. Therefore the electrons are attracted less strongly by the nucleus.
- 2) Fluorine is the most electronegative element, and is assigned an electronegativity of 4.0 on the Pauling scale.
- 3) In other words, the oxidising power (and reactivity) decreases down the Group.



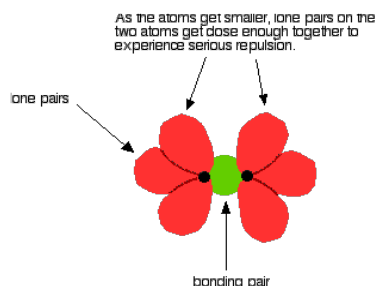
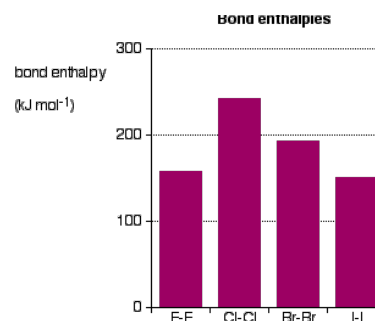
Variation in volatility

- 1) The volatility of halogens **decreases** down the Group. This is because going down the Group, the number of electrons in the halogen molecules increases. More temporary dipoles can be set up and the **strength of van der Waal's forces increases**.
- 2) Hence the boiling point increases and the halogens become less volatile.



Variation in bond enthalpy

- 1) Excluding fluorine, the bond enthalpy of halogens **decreases** down the Group. This is because going down the Group, the **distance between the nucleus and bonding pair of electrons increases**. The bonding electrons are less attracted and as a result, the covalent bond gets weaker. Less energy is required to break the bond.
- 2) The bond enthalpy is exceptionally low because F_2 is a very small molecule with six lone pairs of electrons. The **repulsion** created between these electrons reduces the energy needed to break the covalent bond.



12.2 Reactions of Group VII Elements

Halogens as oxidising agent

- 1) Halogens are powerful oxidising agents. However, the oxidising ability **decreases** down the Group. Therefore, F_2 is the most powerful oxidising agent while I_2 is the weakest.
- 2) This is reflected in their ability to oxidise other halide ions, as follow:

	<i>chlorine, Cl_2</i>	<i>bromine, Br_2</i>	<i>iodine, I_2</i>
<i>Reaction with coloured dyes</i>	bleaches quickly	bleaches slowly	bleaches very slowly
<i>Reaction with chlorides</i>	no reaction	no reaction	no reaction
<i>Reaction with bromides</i>	$Cl_2 + 2NaBr \rightarrow Br_2 + 2NaCl$ (displaces bromine)	no reaction	no reaction
<i>Reaction with iodides</i>	$Cl_2 + 2NaI \rightarrow I_2 + 2NaCl$ (displaces iodine)	$Br_2 + 2NaI \rightarrow I_2 + 2NaBr$ (displaces iodine)	no reaction

Note:

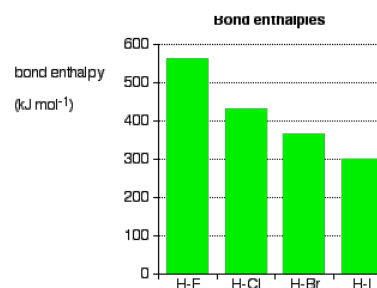
- i. **A halogen can oxidise the halide ion below it** on the Periodic Table, fluorine is excluded in this argument because it is too powerful as an oxidising agent and will oxidise water into oxygen.
- ii. If chlorine is able to displace bromide ion from its aqueous solution, this indicates that chlorine has a higher tendency to be reduced and to accept electrons to form ions.

Reaction with hydrogen gas, H_2

- 1) All halogens react with hydrogen gas to form hydrides, HX .
$$H_2 + X_2 \rightarrow 2HX \quad ; \text{ where } X = \text{A halogen}$$
- 2)
 - i. $H_2(g) + F_2(g) \rightarrow 2HF(g)$; explosive reaction under all temperature
 - ii. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$; explosive reaction under sunlight
 - iii. $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$; slow reaction on heating
 - iv. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; an equilibrium mixture is obtained
- 3) The reactivity of halogens towards hydrogen gas decreases down the Group due to the decrease in oxidising ability of the halogens.

Thermal stability of hydrogen halides, HX

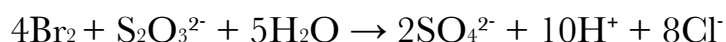
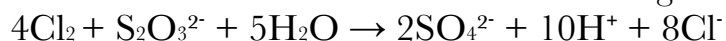
- 1) The thermal stability of the hydrogen halides, HX **decreases** down the Group. This is because the size of the atom increases and so the **strength of the H-X bond decreases**. In other words, the hydrogen halides become less stable on heating going down the Group.



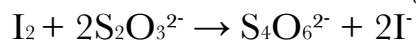
- 2) i. Hydrogen iodide decomposes easily on heating, thick purple fumes of I₂ are observed.
ii. Hydrogen bromide decomposes slightly, little orange-brown of Br₂ is observed.
iii. Hydrogen chloride and fluoride are stable on heating.
- 3) When hydrogen halides decompose, X⁻ ions are oxidised. The ease of oxidation down the Group indicates the increase in reducing ability of X⁻ ion. Hence, I⁻ is the strongest reducing agent while F⁻ is the weakest.

Reaction with aqueous sodium thiosulfate, Na₂S₂O₃

- 1) Chlorine and bromine can oxidise sodium thiosulfate, Na₂S₂O₃ to sodium sulfate, Na₂SO₄. The oxidation number of sulfur changes from +2 to +6.

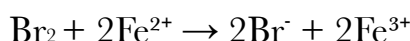
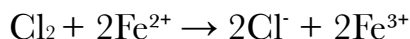


- 2) However, iodine can only oxidise sodium thiosulfate to sodium tetrathionate, Na₂S₄O₆. The oxidation number of sulfur changes from +2 to +2.5.



Reaction with aqueous iron(II) ions, Fe²⁺

- 1) Chlorine and bromine would oxidise Fe²⁺ to Fe³⁺ but not iodine.

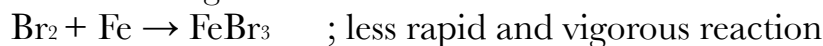


Reaction with iron, Fe

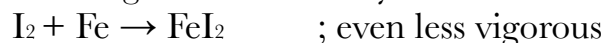
- 1) i. When chlorine gas is passed over hot iron, iron(III) chloride is formed. The oxidation number of iron changes from 0 to +3.



- ii. When bromine vapour is passed over hot iron, iron(III) chloride is formed. The oxidation number of iron changes from 0 to +3.



- iii. When iodine vapour is passed over hot iron, iron(II) chloride is formed. The oxidation number of iron changes from 0 to only +2.



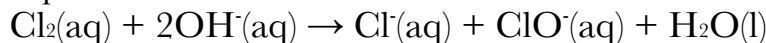
Reaction with hot and cold alkali

- 1) Chlorine undergoes **disproportionation** when it reacts with alkali. In this reaction, chlorine is **simultaneously oxidised and reduced**.

- 2) In cold alkali(15 °C), the reaction is as follow:



The ionic equation is:



- 3) In cold alkali, the oxidation number of chlorine changes from **0** in Cl_2 to **-1** in Cl^- (reduction) and **+1** in ClO^- (oxidation).

- 4) In hot alkali(70 °C), the reaction is as follow:



The ionic equation is:



- 5) In hot alkali, the oxidation number of chlorine changes from **0** in Cl_2 to **-1** in Cl^- (reduction) and **+5** in ClO_3^- (oxidation).

- 6) This reaction is the result of disproportionation of chlorate(I) ions in the presence of heat.



- 7) Bromine and iodine react in a similar manner. However, the bromate(I) and iodate(I) ions formed disproportionate readily at all temperatures.

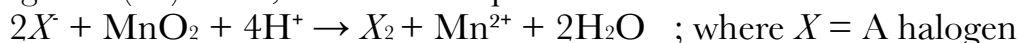
12.3 Reactions of Halide Ions

Introduction to halide ions, X^-

- 1) The halogens are typical non-metals, they:
 - i. form singly charge negative ions, X^- .
 - ii. form ionic compounds with metals and covalent compounds with non-metals.

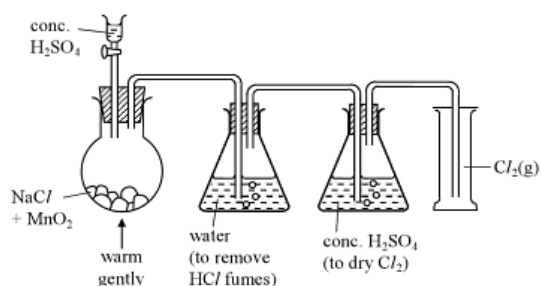
Preparation of halogens in the laboratory

- 1) Halogens can be prepared in the laboratory by the oxidation of X^- ions using manganese(IV) oxide, MnO_2 in the presence of concentrated sulfuric acid.



- 2) The apparatus needed is shown below:

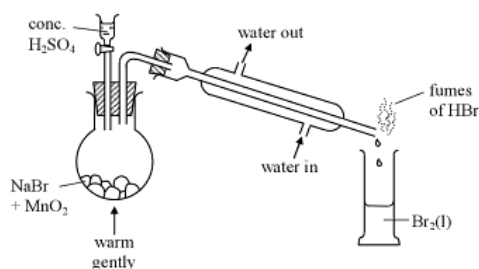
Laboratory preparation of chlorine: $2Cl^- + MnO_2 + 4H^+ \rightarrow Cl_2 + Mn^{2+} + 2H_2O$



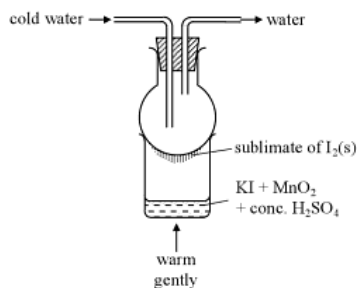
Note:

- i. In each case, hydrogen halide is also formed from the reaction of X^- with H_2SO_4 and must be removed in order to obtain pure halogen.

Laboratory preparation of bromine: $2Br^- + MnO_2 + 4H^+ \rightarrow Br_2 + Mn^{2+} + 2H_2O$



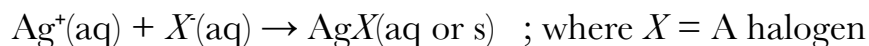
Laboratory preparation of iodine: $2I^- + MnO_2 + 4H^+ \rightarrow I_2 + Mn^{2+} + 2H_2O$



Test for halide ions (reaction with silver ion, Ag^+)

1) Halide ions are colourless in their aqueous solutions and a test is needed to identify their presence.

2) **Silver ions, Ag^+** can be used to test halide ions because the silver halide is formed as precipitate.



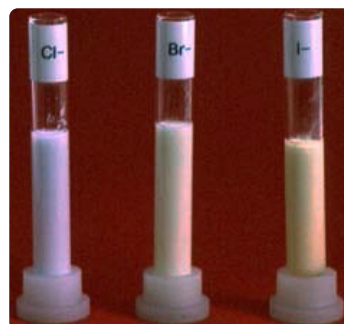
The silver halides formed can be differentiated by:

i. their colour.

ii. their reaction with dilute aqueous ammonia, NH_3 .

3) The test is summarised below: (Fluoride does not form precipitates)

	colour	Reaction with $\text{NH}_3(\text{aq})$
AgCl	white ppt.	$\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \rightarrow [\text{Ag}(\text{NH}_3)_2]^+(\text{aq}) + \text{Cl}^-(\text{aq})$ <i>diammine silver(I) ion</i> (precipitate readily dissolves in $\text{NH}_3(\text{aq})$ to give a colourless solution)
AgBr	cream ppt.	$\text{AgBr}(\text{s}) + 2\text{NH}_3(\text{aq}) \rightarrow [\text{Ag}(\text{NH}_3)_2]^+(\text{aq}) + \text{Br}^-(\text{aq})$ <i>diammine silver(I) ion</i> (precipitate only dissolves in <i>concentrated</i> NH_3 solution)
AgI	yellow ppt.	precipitate <i>insoluble</i> in $\text{NH}_3(\text{aq})$



4) NH_3 is used as a confirmatory test as cream and white precipitate may be hard to distinguish.

5) Alternatively, concentrated sulfuric acid can be used to test halide ions:

ion present	observation
F^-	steamy acidic fumes (of HF)
Cl^-	steamy acidic fumes (of HCl)
Br^-	steamy acidic fumes (of HBr) contaminated with brown bromine vapour
I^-	Some steamy fumes (of HI), but lots of purple iodine vapour (plus various red colours in the tube)

Note:

i. F^- and Cl^- can be differentiated using the silver ion test.

ii. The chemistry of this test is explained next.

Reaction with concentrated sulfuric acid, H₂SO₄

- 1) When halides(NaX) are reacted with concentrated sulfuric acid, the following happens:

	Reaction with conc. H ₂ SO ₄	Observations
Cl ⁻	$\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{HCl} + \text{NaHSO}_4$ <i>steamy fumes</i>	➤ only <i>steamy fumes</i> of HCl(g) produced.
Br ⁻	$\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow \text{HBr} + \text{NaHSO}_4$ $2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$	➤ <i>orange-brown fumes</i> (of Br ₂ and HBr) obtained. ➤ Some of the HBr produced is <i>oxidised</i> by concentrated H ₂ SO ₄ to Br ₂ .
I ⁻	$\text{NaI} + \text{H}_2\text{SO}_4 \rightarrow \text{HI} + \text{NaHSO}_4$ $8\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$	➤ <i>purple vapour</i> of I ₂ (g) obtained. ➤ HI produced is <i>oxidised</i> by concentrated H ₂ SO ₄ to I ₂ .

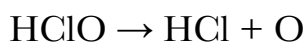
- 2) The **ease of oxidation of halide ions increases** from Cl⁻ to I⁻ because the tendency to be oxidised(the reducing power) increases. The HBr and HI produced are oxidised to Br₂ and I₂ respectively while the HCl produced is not. (HI is oxidised readily while HBr is not)
- 3) To prepare HI or HBr, phosphoric acid, H₃PO₄ is used instead because all halides react to give the corresponding hydrides.
- $$2\text{NaX} + \text{H}_3\text{PO}_4 \rightarrow 2\text{HX} + \text{Na}_2\text{HPO}_4 \quad ; \text{ where } X = \text{A halogen}$$

12.4 Uses of Halogens

- 1) Chlorine is used in the **chlorination of water to kill bacteria**. The chlorine undergoes disproportionation.



Chloric(I) acid, HClO produced decomposes slowly to produce reactive oxygen atoms that kill bacteria in water.



- 2) **Bleach** is an equal mixture of sodium chloride, NaCl and sodium chlorate(I), NaClO. Sodium chlorate(I) is a powerful oxidising agent and bleaches dye and other coloured molecules by oxidising them.

- 3) i. Halogens are also used in **chlorofluorocarbons(CFCs)**. CFCs are widely used as refrigerants, propellants and aerosols. They are also used as solvents for dry cleaning and generating foamed plastics like expanded polystyrene or polyurethane foam.
- ii. Unfortunately, CFCs are largely responsible for destroying the ozone layer. In the high atmosphere, the carbon-chlorine bonds break to give chlorine free radicals and these radicals destroy the ozone. CFCs are now being replaced by less environmentally harmful compounds.
- 4) i. **Plastic PVC**(poly(chloroethene) or polyvinyl chloride) are made from halogen compounds.
- ii. Poly(chloroethene) is made through polymerisation of organic molecules, the organic molecule is chloroethene, CH_2CHCl . These organic molecules join together repeatedly to form the polymer.



- iii. Poly(chloroethene) is used to make a wide range of things including guttering, plastic windows, electrical cable insulation, sheet materials for flooring and other uses, footwear, clothing, and so on.
- 5) Bromine and iodine are often used in the manufacture of dyes and drugs.