CHAPTER 12: Group VII

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.

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

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

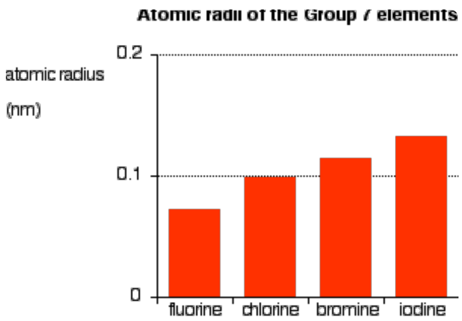
	Colour and state at r.t.	*b.p. / °C*	*Solubility*	
			in water	*in organic solvent*
F_2	pale yellow gas	–188	–	–
Cl_2	yellow-green gas	–35	moderately soluble	yellow solution
Br_2	dark red liquid	58	slightly soluble	orange-brown solution
I_2	black solid	183	insoluble	violet/purple solution

Note:

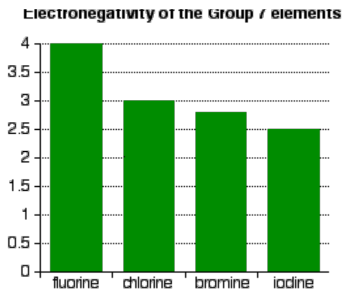
i. Bromine is a dark red liquid but forms reddish-brown gas.
ii. Iodine is a black solid but forms a **purple vapour** on gentle heating.
iii. The trend is the halogens get **darker** going down the Group.
iv. Iodine is insoluble in water but it dissolves in potassium iodide, KI solution due to the formation of I_3^- ion.
v. In organic solvents, halogens exist as free molecules, X_2.

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

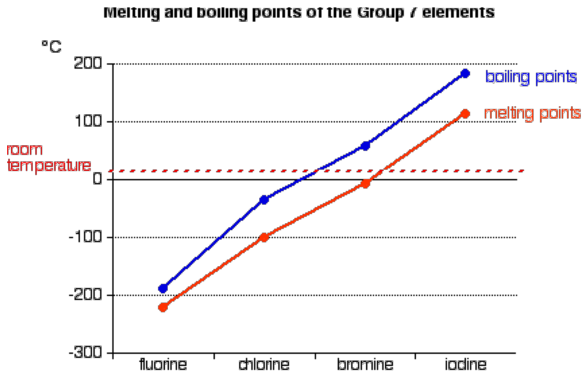


1) The electronegativity of halogens **decreases** down the Group. This is because going down the Group, the distance between the nucleus and bonding electrons increases. Therefore the electrons are attracted less strongly by the nucleus.

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.

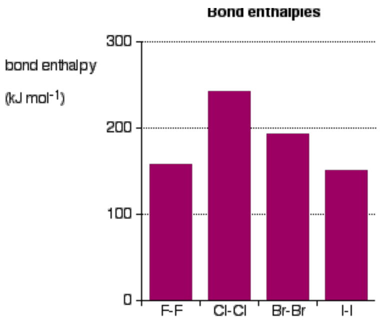
Variation in volatility



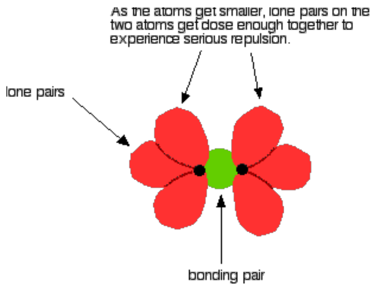
1) The volatility of halogens **decreases** down the Group. This is because going down the Group, the number of electrons in the halogen molecules increases. More temporary dipoles can be set up and the **strength of van der Waal's forces increases**.

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.



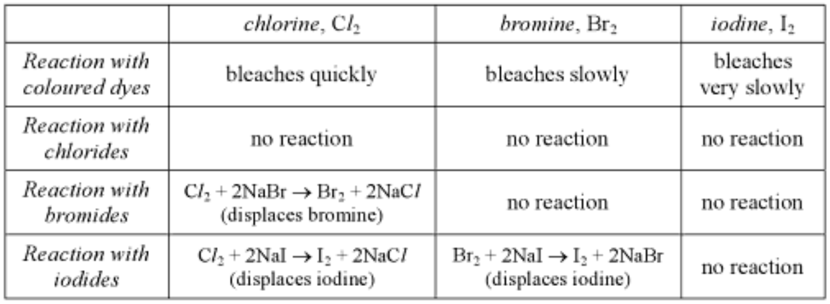
2) The bond enthalpy is exceptionally low because F_2 is a very small molecule with six lone pairs of electrons. The **repulsion** created between these electrons reduces the energy needed to break the covalent bond.

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:



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

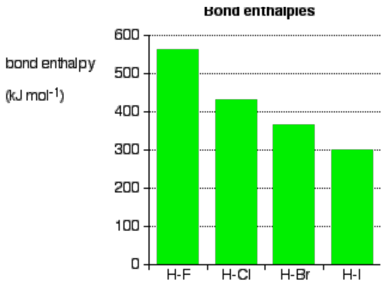
1) All halogens react with hydrogen gas to form hydrides, H*X*.

$$H_2 + X_2 \rightarrow 2HX \quad \text{; where } X = \text{A halogen}$$

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, H*X*



1) The thermal stability of the hydrogen halides, H*X* **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 I_2 are observed.
   ii. Hydrogen bromide decomposes slightly, little orange-brown of Br_2 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, $Na_2S_2O_3$

1) Chlorine and bromine can oxidise sodium thiosulfate, $Na_2S_2O_3$ to sodium sulfate, Na_2SO_4. The oxidation number of sulfur changes from +2 to +6.

$$4Cl_2 + S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8Cl^-$$
$$4Br_2 + S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8Cl^-$$

2) However, iodine can only oxidise sodium thiosulfate to sodium tetrathionate, $Na_2S_4O_6$. The oxidation number of sulfur changes from +2 to +2.5.

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Reaction with aqueous iron(II) ions, Fe^{2+}

1) Chlorine and bromine would oxidise Fe^{2+} to Fe^{3+} but not iodine.

$$Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$$
$$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$$

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.

$Cl_2 + Fe \rightarrow FeCl_3$; rapid and vigorous reaction

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

$Br_2 + Fe \rightarrow FeBr_3$; less rapid and vigorous reaction

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.

$I_2 + Fe \rightarrow FeI_2$; even less vigorous

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:

$$Cl_2(aq) + 2NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$$

The ionic equation is:

$$Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

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:

$$3Cl_2(aq) + 6NaOH(aq) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$$

The ionic equation is:

$$3Cl_2(aq) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$$

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.

$$3ClO^-(aq) \rightarrow 2Cl^-(aq) + ClO_3^-$$

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^-

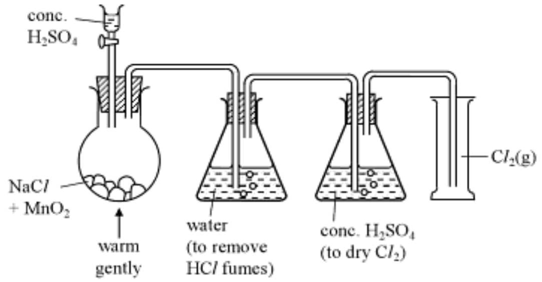
1) The halogens are typical non-metals, they:
   i. form singly charge negative ions, X^-.
   ii. form ionic compounds with metals and covalent compounds with non-metals.

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.
   $2X^- + MnO_2 + 4H^+ \rightarrow X_2 + Mn^{2+} + 2H_2O$; where X = A halogen

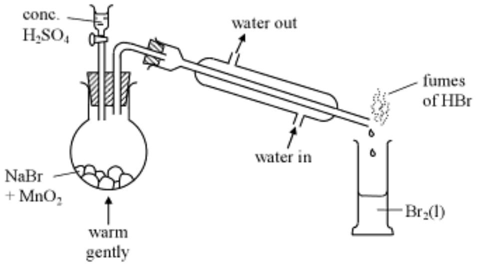
2) The apparatus needed is shown below:

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

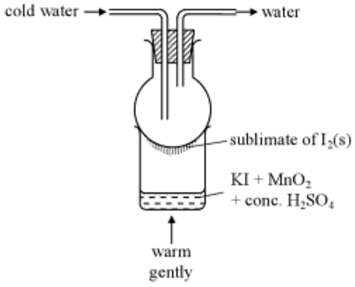


Note:
i. In each case, hydrogen halide is also formed from the reaction of X^- with H_2SO_4 and must be removed in order to obtain pure halogen.

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.

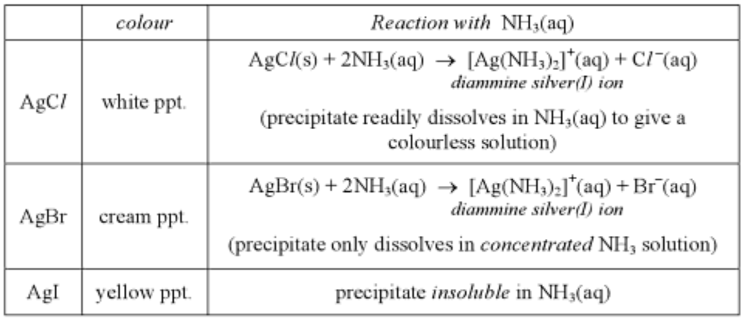
$$Ag^+(aq) + X^-(aq) \rightarrow AgX(aq\ or\ s) \quad ;\ where\ X = A\ halogen$$

The silver halides formed can be differentiated by:

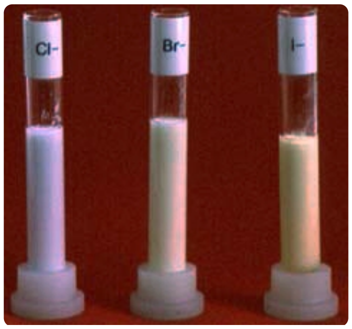
i. their colour.

ii. their reaction with dilute aqueous ammonia, NH_3.

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

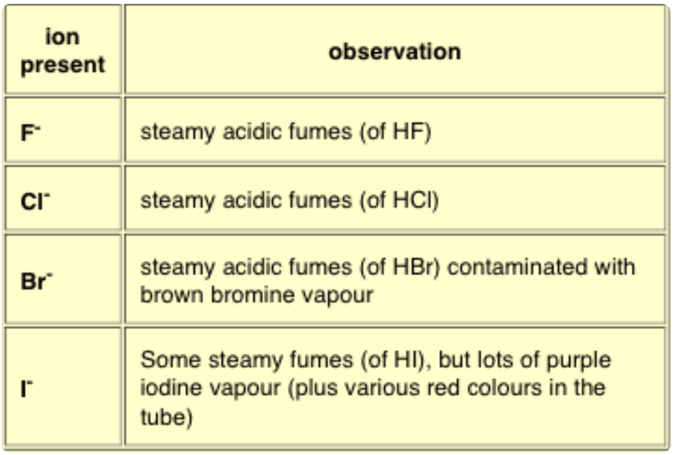


	colour	*Reaction with* $NH_3(aq)$
$AgCl$	white ppt.	$AgCl(s) + 2NH_3(aq) \rightarrow \underbrace{[Ag(NH_3)_2]^+(aq)}_{\textit{diammine silver(I) ion}} + Cl^-(aq)$ (precipitate readily dissolves in $NH_3(aq)$ to give a colourless solution)
AgBr	cream ppt.	$AgBr(s) + 2NH_3(aq) \rightarrow \underbrace{[Ag(NH_3)_2]^+(aq)}_{\textit{diammine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



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)

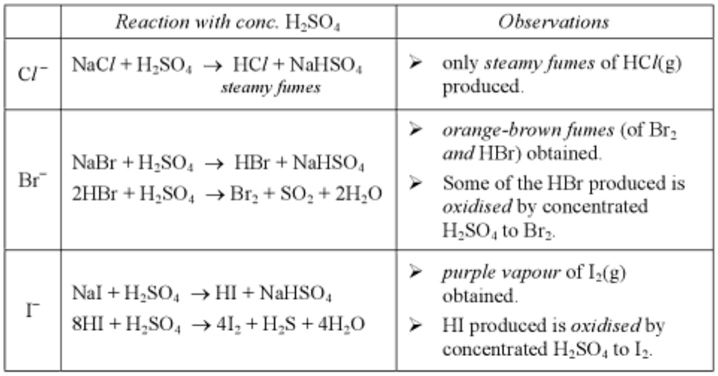
Note:

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, H_2SO_4

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



	Reaction with conc. H_2SO_4	*Observations*
Cl^-	$NaCl + H_2SO_4 \rightarrow \underset{\textit{steamy fumes}}{HCl} + NaHSO_4$	➢ only *steamy fumes* of $HCl(g)$ produced.
Br^-	$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$ $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$	➢ *orange-brown fumes* (of Br_2 *and* HBr) obtained. ➢ Some of the HBr produced is *oxidised* by concentrated H_2SO_4 to Br_2.
I^-	$NaI + H_2SO_4 \rightarrow HI + NaHSO_4$ $8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$	➢ *purple vapour* of $I_2(g)$ obtained. ➢ HI produced is *oxidised* by concentrated H_2SO_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 Br_2 and I_2 respectively while the HCl produced is not. (HI is oxidised readily while HBr is not)

3) To prepare HI or HBr, phosphoric acid, H_3PO_4 is used instead because all halides react to give the corresponding hydrides.

$$2NaX + H_3PO_4 \rightarrow 2HX + Na_2HPO_4 \quad ; \text{where } X = \text{A halogen}$$

12.4 Uses of Halogens

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

$$Cl_2(aq) + H_2O(l) \rightarrow HCl(aq) + HClO(aq)$$

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

$$HClO \rightarrow HCl + O$$

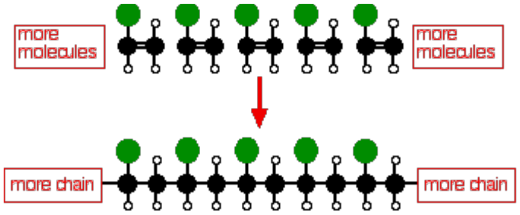
2) **Bleach** is an equal mixture of sodium chloride, NaCl and sodium chlorate(I), NaClO. Sodium chlorate(I) is a powerful oxidising agent and bleaches dye and other coloured molecules by oxidising them.

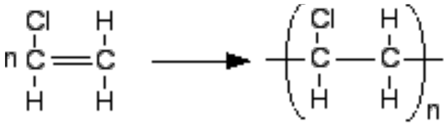
3) i. Halogens are also used in **chlorofluorocarbons(CFCs)**. CFCs are widely used as refrigerants, propellants and aerosols. They are also used as solvents for dry cleaning and generating foamed plastics like expanded polystyrene or polyurethane foam.

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.