

## CHAPTER

## 5

**THE HALOGENS AND  
THE NOBLE GASES****In this chapter you will learn**

1. The electronic configurations and the occurrence of halogens, the peculiar behaviour of fluorine.
2. The volatility of halogens and its explanation in terms of van der Waal's forces.
3. The relative reactivities of halogens as oxidizing agents.
4. The properties of hydrogen halides, oxides and oxyacids of halogens.
5. The comparison of thermal stability of hydrides in terms of bond energies.
6. Reaction of chlorine with sodium hydroxide (hot/cold).
7. The preparation and reaction of bleaching powder.
8. The commercial uses of halogens and their compounds as bleaches, refrigerants, aerosols and anaesthetics.
9. The electronic configurations, physical properties, inertness and isolation of noble gases from air.
10. The properties of oxides, fluorides and oxyfluorides of xenon

**5.1 INTRODUCTION**

The elements fluorine (F), chlorine(Cl), bromine(Br), iodine(I) and astatine(At) are called halogens. These elements are called the halogens from Greek *hals*, "salt" and *gennan*, "to form or generate", because they are literally the salt formers. The halogen elements form a group of very reactive non-metals and are quite similar to each other in their chemical properties. First four elements are the common elements of the halogen family but astatine is a rare halogen. It is radioactive and its most stable isotope has a half life of only 8.3 hrs.

Halogens exist as discrete diatomic molecules in all phases (gas, liquid or solid). Fluorine and chlorine are gases of pale yellow and greenish yellow colours respectively at room temperature and pressure. Bromine is a liquid of red-brown colour and iodine is a metallic-appearing shiny greyish black solid. The halogens have irritating odours, and they attack the skin. Bromine in particular causes burns that heal slowly. The outer shell of halogens have the configuration  $ns^2 np^5$  (one electron short of the stable octet of the noble gases). The electronic configurations and the important physical properties of the halogens are given in the Table 5.1.



The ionization energy data of the halogens shows that the fluorine atom holds its electrons tightly whereas the electrons are least tightly bound in iodine. The trend can be correlated with the sizes of the halogen atoms as shown in the Table 5.1.

The electron affinity values of halogens are large and negative, that is why halogens gain electrons readily. They have large, positive standard electrode potentials and their electronegativities are also fairly high.

The intermolecular attraction is greater in the larger molecules having greater masses. Due to their large size, the van der Waal's forces in iodine molecules are stronger than in the smaller molecules of the other halogens.

**Table 5.1 The Electronic Configurations and the Important Physical Properties of the Halogens.**

Properties	Fluorine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Electronic configuration	[He]2s <sup>2</sup> 2p <sup>5</sup>	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	[Ar]3d <sup>10</sup> ,4s <sup>2</sup> ,4p <sup>5</sup>	[Kr]4d <sup>10</sup> ,5s <sup>2</sup> ,5p <sup>5</sup>
Physical appearance	Pale Yellow gas	Greenish yellow gas	Red-brown liquid	Shiny greyish black solid
Ionization energy(kJ mol <sup>-1</sup> )	1681	1251	1143	1009
Electron affinity, (kJ mol <sup>-1</sup> )	-322	-349	-325	-295
Electronegativity	4.00	3.00	2.8	2.5
Ionic radius (pm)	133	181	196	220
Covalent radius (pm)	72	100	114	133
Melting point (°C)	-219	-101	-7.2	114
Boiling point (°C)	-188	-34.1	59.5	185
Density (g/cm <sup>3</sup> )	0.00181	0.00321	3.12	4.93
Oxidation states	-1	-1,+1,+3,+5,+7	-1,+1,+3,+5,+7	-1,+1,+3,+5,+7
Bond energy (kJ mol <sup>-1</sup> ) (X-X)	154.80	242.67	192.46	150.6

## 5.2 OCCURRENCE

Elements with the higher values of electronegativity usually exist as negative ions, and those with the lower values of electronegativity exist as positive ions. Elements with intermediate values of electronegativity are often found as ions or molecules or in free (elemental) form.

None of the halogens is found in free form in nature. The halogens exist in nature primarily in the form of compounds. Their most common state is the halide ions F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>. These halides are soluble in water and are found in sea, in salt lakes and as underground beds of salt.



Fluorine	Chlorine
Fluorspar $\text{CaF}_2$	Halite $\text{NaCl}$
Cryolite $\text{Na}_3\text{AlF}_6$	(Salt beds, brine wells, sea water)
Fluoroapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$	Carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Bromine	Iodine
Brine wells, sea water, $\text{NaBr}$ , $\text{KBr}$ , $\text{MgBr}_2$ ,	$\text{NaIO}_3$ , $\text{NaIO}_4$ deposits in Chile brine wells.

### 5.3 PECULIAR BEHAVIOUR OF FLUORINE

The halogens form a homologous series but fluorine differs from the other halogens in many respects which is due to:

- Small size of F atom and of  $\text{F}^-$  ion.
- High first ionization energy and electronegativity.
- Low dissociation energy of  $\text{F}_2$  molecule as compared to  $\text{Cl}_2$  and  $\text{Br}_2$ .
- Restriction of the valence shell to an octet.
- Direct combination with inert gases.

Due to the small size of the F atom (or  $\text{F}^-$  ion), there will be a better overlap of orbitals and consequently leads to shorter and stronger bonds with elements other than O, N and itself. Ionic fluorides have higher lattice energies than the other halides and these values are responsible for the insolubility of the fluorides of Ca, Mg, Ba, Sr and lanthanides in water. Due to the low dissociation energy of fluorine molecule, it is highly reactive. The other halogens react slowly under similar conditions. The fluorides are, however, more stable with respect to dissociation into elements.

Due to the restriction of valence shell to an octet, many fluoro compounds show inertness, e.g.  $\text{CF}_4$  and  $\text{SF}_6$ . Also due to this restriction, fluorine remains restricted to  $-1$  oxidation state.

Fluorine is the only element that combines directly with noble gases like Kr, Xe, and Rn forming their fluorides.

### 5.4 OXIDIZING PROPERTIES

#### Relative Reactivities of the Halogens as Oxidizing Agents

All the free halogens act as oxidizing agents when they react with metals or nonmetals. The reactant elements acquire positive oxidation state in the compounds formed.

On forming ionic compounds with metals, the halogens gain electrons and are converted to negative halide ions.



The oxidizing power of halogens decreases with increase in atomic number. Fluorine has the highest oxidizing power and iodine the least. The order of decreasing power as an oxidizing agent is  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .



The oxidizing power of halogens depends upon the following factors:

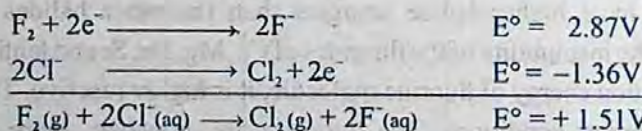
- (i) Energy of dissociation
- (ii) Electron affinity of atoms
- (iii) Hydration energies of ions
- (iv) Heats of vapourization (for Br<sub>2</sub> and I<sub>2</sub>)

If a halogen has a low energy of dissociation, a high electron affinity and a higher hydration energy of its ions, it will have a high oxidizing power.

Oxidizing power of F<sub>2</sub> is higher, because it has low energy of dissociation and higher hydration energy of its ions. Due to the relative strength as oxidizing agents, it is possible for each free halogen to oxidize the ions of other halogens next to it in the family. Standard electrode potential measures oxidizing power.

	F <sub>2</sub>	Cl <sub>2</sub>	Br <sub>2</sub>	I <sub>2</sub>
Standard reduction potential, [E°(V)]	+2.87	+1.36	+1.07	+0.54
X <sub>2</sub> + 2e <sup>-</sup> → 2X <sup>-</sup>				

Fluorine can oxidize all the halide ions to molecular halogens. (A reaction will occur if the value of E° is positive) Iodine being a weak oxidizing agent cannot oxidize chloride or bromide ion.



In the similar way, chlorine will oxidize both bromide and iodide ions, while bromine can oxidize only iodide ion.



Fluorine and chlorine can oxidize various coloured dyes to colourless substances, e.g. litmus and universal indicator can be decolourized when exposed to fluorine or chlorine. When used for bleaching, chlorine acts as an oxidizing agent.

## 5.5 COMPOUNDS OF HALOGENS

### 5.5.1 Hydrides (hydrogen halides, HX)

All halogens react with hydrogen forming hydrides. The reaction of molecular hydrogen and fluorine is very fast and explosive. With chlorine, molecular hydrogen reacts in the presence of sunlight. Bromine and iodine react with molecular hydrogen at a higher temperature. The reaction with iodine is very slow and reversible. Direct combination is used as a preparative method only for HCl and HBr. Hydrogen fluoride and hydrogen chloride can also be obtained by the action of concentrated sulphuric acid on fluorides and chlorides, but analogous reactions with bromides and iodides result in partial oxidation of the hydrogen halide to the free halogen.





### Properties of Hydrogen Halides

HF is a colourless volatile liquid whereas other hydrogen halides (HCl, HBr, HI) are colourless gases at room temperature. They give fumes in moist air. They are strong irritants.

Hydrogen fluoride attacks glass and has found applications as a non-aqueous solvent. It can be handled in teflon (polytetrafluoroethylene) containers or if absolutely dry, in copper or stainless- steel vessels kept under vacuum. Pure liquid HF is strongly hydrogen bonded and is a viscous liquid. Its viscosity is less than that of water due to the absence of a three-dimensional network of H-bonds which occur in H<sub>2</sub>O. Hydrogen bonding is also responsible for the association of HF molecules in the vapour phase. Various test results indicate that gaseous HF consists of an equilibrium mixture of monomers and cyclic hexamers, Fig. 5.2.

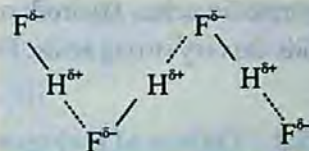


Fig 5.2 Hydrogen bonding in HF



Chain polymers may also exist under certain conditions. Chains and rings of HF are of various sizes, some of these persist in the vapour phase as well. Some of the physical properties of hydrogen halides are given in Table 5.2.

Table 5.2 Some Physical Properties of Hydrogen Halides

Properties	HF	HCl	HBr	HI
Melting points(°C)	-83.8	-114.2	-86.9	-50.8
Boiling points (°C)	19.5	-85.0	-66.7	-35.3
Heat of fusion at M.P. (kJ/mol)	4.58	1.99	2.41	2.87
Heat of vaporization at B.P. (kJ/mol)	30.3	16.2	17.6	19.7
Heat of formation /kJmol <sup>-1</sup> ΔH <sub>f</sub>	-270.0	-92.0	-36.0	+26.0
Bond energy (kJ/mol <sup>-1</sup> )	566	431	366	299
H-X Bond length (pm)	92	128	141	160
Dissociation into elements at 1000°C (%)	0	0.014	0.5	33
Dipole moment (Debye)	1.8	1.1	0.8	0.4

Melting points, boiling points, heats of fusion and heats of vapourization generally increase regularly from HCl to HI. The HF has much higher values for these properties due to hydrogen bonding. A very high boiling point of hydrogen fluoride is a major evidence of the presence of hydrogen bonding among its molecules. The relative volatility of HCl, HBr and HI reflects the strengthening of the van der Waal's forces due to increasing size of halogens. Since the dipole moment of molecules decreases from HCl to HI, probably dipole-induced dipole forces play an important role in the intermolecular binding of the heavier HX molecules.

The strength of the hydrogen halogen bond is very high in HF. It decreases with



increasing size of the halogen atom. The bond strength is reflected in the case of dissociation of hydrogen halides at elevated temperatures.

HF, HCl, HBr and HI act as reducing agents in the following order:



Hydrogen iodide is a strong reducing agent. In redox reactions the hydrogen halides are oxidized to elemental halogens, e.g.



In water, hydrogen halides give hydrofluoric, hydrochloric, hydrobromic and hydroiodic acids. Hydrofluoric acid is a weak acid due to limited ionization. The other three acids are very strong acids. The acidic strength increases in the order:



### 5.5.2 Oxides of Halogens

The halogens do not react directly with oxygen. With the help of some indirect methods, following oxides of group VIIA elements have been made.

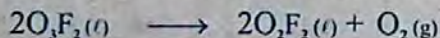
Table 5.3 Oxides of Halogens

FLUORINE	CHLORINE	BROMINE	IODINE
Oxygen difluoride, $\text{OF}_2$ Dioxygen difluoride, $\text{O}_2\text{F}_2$ Trioxygen difluoride, $\text{O}_3\text{F}_2$	Dichlorine monoxide, $\text{Cl}_2\text{O}$ Chlorine dioxide, $\text{ClO}_2$ Chlorine hexaoxide, $\text{Cl}_2\text{O}_6$ Chlorine heptaoxide, $\text{Cl}_2\text{O}_7$	Bromine monoxide, $\text{Br}_2\text{O}$ Bromine dioxide, $\text{BrO}_2$ Bromine trioxide, $\text{BrO}_3$ , $(\text{Br}_2\text{O}_3)$	Iodine tetraoxide, $\text{I}_4\text{O}_4$ Iodine iodate, $\text{I}_2\text{O}_5$ Iodine pentoxide, $\text{I}_2\text{O}_5$

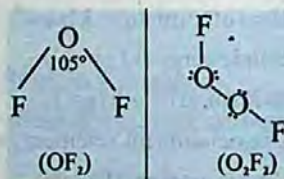
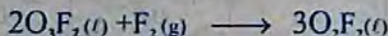
#### Oxides of Fluorine

##### Tri oxygen Difluoride, $\text{O}_3\text{F}_2$

This oxide can be prepared when a mixture of fluorine and oxygen is subjected to electric discharge. At  $363^\circ\text{C}$ , it is a dark red viscous liquid but turns to reddish brown solid at  $350^\circ\text{C}$ . On decomposition it gives oxygen and other oxide of fluorine.



$\text{O}_3\text{F}_2$  reacts with  $\text{F}_2$  in the presence of electric discharge to produce  $\text{O}_2\text{F}_2$



Structure of  $\text{OF}_2$  and  $\text{O}_2\text{F}_2$

#### OXIDES OF CHLORINE

The oxides of chlorine are generally unstable. It is not possible to synthesize them by direct combination of the elements  $\text{Cl}_2$  and  $\text{O}_2$ . They have extensive industrial use as commercial bleaching agents for wood, paper-pulp and for water treatment.

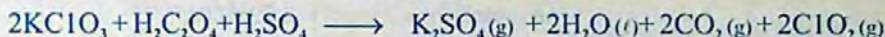
##### 1. Chlorine dioxide, $\text{ClO}_2$

It is a pale yellow gas. It is prepared by reducing  $\text{NaClO}_3$  with  $\text{NaCl}$  or  $\text{SO}_2$  or  $\text{CH}_3\text{OH}$  in strongly acidic solution.





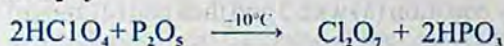
$\text{ClO}_2$  can also be prepared by the action of concentrated  $\text{H}_2\text{SO}_4$  on  $\text{KClO}_3$ . This reaction is violent. To control the reaction oxalic acid should be added.



$\text{ClO}_2$  explodes into  $\text{Cl}_2$  and  $\text{O}_2$  on warming. It is soluble in water and is stable in dark. It decomposes slowly in  $\text{H}_2\text{O}$  to  $\text{HCl}$  and  $\text{HClO}_3$ . It is a paramagnetic substance. It is used as an antiseptic, for purification of water and to bleach cellulose material.

## 2. Chlorine Heptaoxide, $\text{Cl}_2\text{O}_7$

$\text{Cl}_2\text{O}_7$  is an anhydride of perchloric acid ( $\text{HClO}_4$ ). It can be obtained at  $-10^\circ\text{C}$  by dehydration of  $\text{HClO}_4$  with  $\text{P}_2\text{O}_5$ .

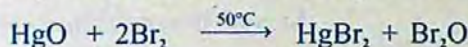


## OXIDES OF BROMINE

Oxides of bromine are dark volatile liquids with low thermal stability.

### Bromine Monoxide $\text{Br}_2\text{O}$

It can be prepared by the reaction of bromine vapours with mercuric oxide.



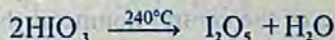
$\text{Br}_2\text{O}$  can also be prepared by treating the suspension of mercuric oxide in  $\text{CCl}_4$  with bromine. It is stable in dark in  $\text{CCl}_4$  at  $-20^\circ\text{C}$ . It has oxidizing properties.

## OXIDES OF IODINE

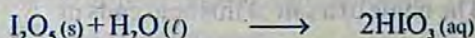
Out of all the oxides of iodine only iodine pentoxide ( $\text{I}_2\text{O}_5$ ) is important. The other compounds,  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_6$ , are salt like and are considered as iodine-iodates.

### Iodine Pentoxide $\text{I}_2\text{O}_5$

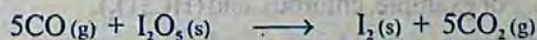
It can be prepared by heating iodic acid at  $240^\circ\text{C}$ .



It is a white crystalline solid, stable up to  $300^\circ\text{C}$ . It has a polymeric structure. It is insoluble in organic solvents. It forms iodic acid with water.



It reacts with  $\text{H}_2\text{S}$ ,  $\text{HCl}$  and  $\text{CO}$  as an oxidizing agent. It is used for the quantitative analysis of  $\text{CO}$ .



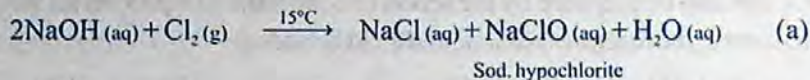
## 5.5.3 Reactions of Chlorine with Cold and Hot $\text{NaOH}$

The reactions of chlorine with cold and hot  $\text{NaOH}$  are examples of "Disproportionation reactions".

A reaction in which a species (molecule, atom or ion) is simultaneously oxidized and reduced, is called a "disproportionation reaction".

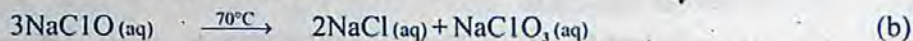


In cold state  $15^{\circ}\text{C}$  chlorine will react with  $\text{NaOH}$  (aq) to form hypochlorite and a halide.

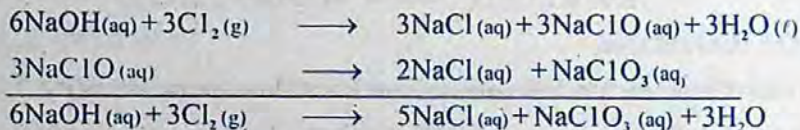


The reaction is a disproportionation reaction, because the zero oxidation state of chlorine atom in  $\text{Cl}_2$  is converted to -1 in chloride and +1 in hypochlorite.

Sodium hypochlorite which is produced in cold state in the above reaction, decomposes forming sodium chloride and sodium chlorate at  $70^{\circ}\text{C}$ .



The reaction (b) involves the disproportionation of hypochlorite ion. To balance overall reaction in hot state, multiply equation (a) with 3 and then add (a) and (b).



The above two reactions (a) and (b) show that chlorine atoms are both reduced and oxidized.

### 5.5.4 Oxyacids

An important class of the compounds of the halogens is the oxygen containing acids and their salts.

No oxygen containing stable acid of fluorine is known ( $\text{HOF}$  is prepared recently, but it is highly unstable). Other halogens form oxyacids though most of them cannot be isolated in pure form and are stable only in aqueous solutions in the form of their salts.

A system of nomenclature for these acids and their salts is based on the oxidation state of the halogen atom. According to this system, characteristic prefixes and suffixes are attached to a stem that is derived from the name of the central nonmetal (halogen) atom. The system is as follows:

1. Some common acid is arbitrarily called the \_\_\_\_\_ic acid (e.g.  $\text{HClO}_3$  is designated as chloric acid). The name of a salt of this acid ends in \_\_\_\_\_ate.
2. An acid whose parent atom has an oxidation state next lower than the \_\_\_\_\_ic acid (one less oxygen atom) is called \_\_\_\_\_ous acid and the name of the salt of this acid ends in \_\_\_\_\_ite. For example, chlorous acid ( $\text{HClO}_2$ ).
3. The acid in which the oxidation state of the parent atom is higher than it is in the \_\_\_\_\_ic acid (one more oxygen atom) is called per \_\_\_\_\_ic acid. A salt of this acid is a per \_\_\_\_\_ate salt. For example, perchloric acid ( $\text{HClO}_4$ ).
4. An acid in which the oxidation state of the parent atom is lower than it is in the \_\_\_\_\_ous acid is called hypo \_\_\_\_\_ous acid and a salt of this acid is a hypo \_\_\_\_\_ite salt.



For example, hypochlorous acid (HClO).

5. The root of the name of the acid or the salt indicates the parent atom.

Table 5.4 shows the oxyacids of halogens (other than fluorine)

Table 5.4 Oxyacids of Halogens

Oxidation state of halogen	Formulae of the oxyacids of halogens			General names of	
	Chlorine	Bromine	Iodine	Oxyacids	Salts of oxyacids
+1	HClO	HBrO	HIO	Hypohalous acid	Hypo__ite
+3	HClO <sub>2</sub>	-----	-----	Halous acid	__ite
+5	HClO <sub>3</sub>	HBrO <sub>3</sub>	HIO <sub>3</sub>	Halic acid	__ate
+7	HClO <sub>4</sub>		HIO <sub>4</sub> , H <sub>5</sub> IO <sub>6</sub>	Perhalic acid	Per__ate

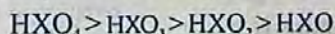
It is evident from the above given formulae of the oxy acids that the halogen serves as a central atom to which one or more oxygen atoms are covalently bonded. These bonds are polar in character due to the electronegativity difference between halogen and oxygen.

The increase in the oxidation state of the halogen from +1 to +7 is accompanied by:

- an increase in the thermal stability of the acid
- the decrease in oxidizing power of the acid
- the increase in acidic strength of the acid

The more the number of oxygen atoms in the series of oxyacids of a halogen, the greater is the thermal stability.

The acid strength increases with the increase in the number of oxygen atoms. As the oxidation state of the halogen increases, the bonding electrons are shifted away from the H-atom and the tendency of the molecule to lose a proton increases. This accounts for the change of strength of oxyacids. The oxyacids of halogens show their strength in the order given below:



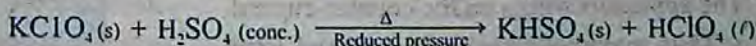
An oxyacid molecule contains hydrogen linked to the halogen through an oxygen atom.

The oxyacids of chlorine are stronger than the corresponding oxyacids of bromine which are, in turn, stronger than the corresponding oxyacids of iodine. It is due to decrease in the electronegativity and increase in the size of the halogen.

We will discuss perchloric acid (HClO<sub>4</sub>) only at this stage.

### PERCHLORIC ACID (HClO<sub>4</sub>)

Perchloric acid (HClO<sub>4</sub>) is commonly obtained in aqueous solution. Pure anhydrous compound can be prepared by distilling a mixture of potassium perchlorate (KClO<sub>4</sub>) and conc. H<sub>2</sub>SO<sub>4</sub> under reduced pressure.



Perchloric acid is a colourless hygroscopic liquid. At normal pressure it freezes at -112°C and boils with decomposition at 90°C.



In the cold and dilute state, perchloric acid is a very weak oxidizing agent but when hot and concentrated its oxidizing power is enhanced. Dissolving power of perchloric acid is enhanced due to its oxidizing strength. Perchloric acid is the strongest of all the acids in an aqueous medium.

Pure perchloric acid decomposes explosively when heated. That is why it is stored and used as 67% solution in water. Perchloric acid reacts with organic substances violently.

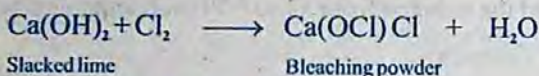
Due to its oxidizing effect, acidic strength and solubility of its salts, it is considered as a valuable analytical reagent.

### 5.5.5 Bleaching Powder, (Ca(OCl)Cl)

Bleaching powder can be manufactured by the action of chlorine on dry slaked lime using any one of the following methods:

- Hasenclever's method (old method)
- Beckmann's method (modern method)

The reaction in both the cases will be:



#### (1) Hasenclever's Method

The apparatus used in this method consists of 4 to 8 iron cylinders placed one above the other horizontally. They are interconnected and provided with stirrers. The slaked lime is added in through a hopper in the upper cylinder and is transported from one cylinder to the other with rotating stirrers. Chlorine introduced into the lowest cylinder rises up and reacts with slaked lime to form bleaching powder, which is collected through the outlet in the lowest cylinder.

#### (2) Beckmann's Method

In this method a cast iron tower with eight horizontal shelves is used. In each shelf there is a rotating rake.

Powdered slaked lime is introduced through hopper at the top with compressed air. A mixture of hot air and chlorine is introduced from the base of the tower. The slaked lime is pushed down by the rotating rakes while chlorine rises up. Reaction between slaked lime and chlorine produces bleaching powder which is collected at the bottom of the tower, Fig. 5.3.

The apparatus works on the counter-current principle. Thus maximum reaction of slaked lime and chlorine is brought about with very little loss of

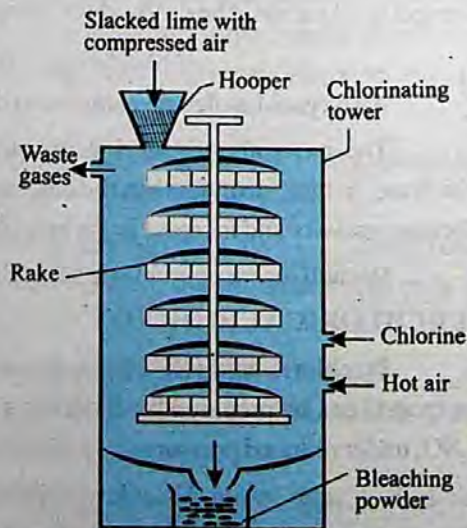


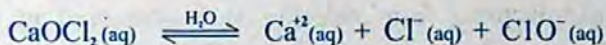
Fig. 5.3 Beckmann's Method



chlorine. Bleaching powder should always be packed in air tight containers to avoid the loss of chlorine.

Bleaching powder is a yellowish white powder with strong smell of chlorine. Some of its chemical properties are given below.

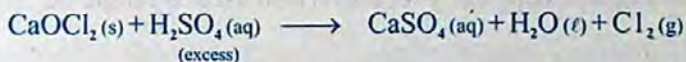
1. It is an oxidizing agent. This property is due to the generation of hypochlorite ion ( $\text{OCl}^-$ ) in water.



2. With dilute acid it gives hypochlorous acid.



3. If excess of an acid (weak or strong) is added to bleaching powder, chlorine is given out.

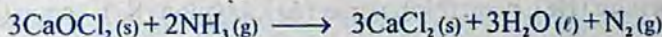


The amount of chlorine thus set free is called "available chlorine". The activity of bleaching powder is measured in terms of available chlorine. The average percentage of available chlorine in bleaching powder is 35-40 percent. The bleaching action of bleaching powder is due to its oxidative character.

4. It oxidizes HCl, HBr and HI giving the corresponding halogens.



5. It oxidizes ammonia to nitrogen



6. Calcium hypochlorite reacts with carbon dioxide to form calcium carbonate and release chlorine.



### Uses

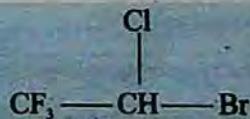
Bleaching powder is used:

- (i) for the laboratory preparation of chlorine and oxygen. It is also used in the manufacture of chloroform.
- (ii) as a disinfectant and in the sterilization of water.
- (iii) for making unshrinkable wool.
- (iv) for bleaching cotton, linen and paper pulp. (Delicate fabrics like wool, silk etc. cannot be bleached with it as these could be damaged by chlorine).

## 5.6 COMMERCIAL USES OF HALOGENS AND THEIR COMPOUNDS

Fluorine is used for the preparation of freons. Freon is the commercial name of low molecular mass fluorochlorocarbons,  $\text{CCl}_2\text{F}_2$ ,  $\text{CClF}_3$ . These are being used as refrigerants and aerosol propellants.

Fluorine is used to prepare Teflon  $(-\text{CF}_2-\text{CF}_2)_n$ . It is a polymerized tetrafluoro ethylene compound. It is a valuable plastic



**Halothane**



which resists the action of oxidants, acids and alkalis. Corrosion proof parts of machinery are made of it. It is used for coating the electrical wiring. Teflon is also used as a non-stick coating for cooking pans. Halothane is used as an anaesthetic.

Fluorides in toothpastes build a protective coating on teeth.

Chlorine is used in the manufacture of bleaching powder. It is used as a disinfectant in swimming pools and water treatment plants. A number of antiseptics, insecticides, weedkillers and herbicides are manufactured from chlorine. It is also used in the manufacture of hydrochloric acid, which is the cheapest industrial acid. Chlorine is also used in the manufacture of polyvinyl chloride (PVC) plastics. Chloroform and carbon tetrachloride are prepared from chlorine which are used as solvents.

Ethylene dibromide ( $C_2H_4Br_2$ ) is added to leaded gasoline to save the engine from lead oxide and lead sulphate deposits. Bromine is also used as fungicide. Silver bromide is used in photography.

The major applications of iodine are in pharmaceutical industry. It is used as disinfectant and germicide. Tincture of iodine and iodox are popular preparations of iodine.

Diet with insufficient iodide ions leads to an enlargement of the thyroid (Goiter). To ensure the presence of iodide ion in the diet, sodium or potassium iodide is added to the common salt which is known as iodized salt.

## 5.7 NOBLE GASES

### 5.7.1 Introduction

The elements helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) are placed in the zero group or group VIIIA of the periodic table. All the elements of this group are colourless and odourless monoatomic gases which can be liquefied and solidified. These are called noble gases or sometime known as rare gases. The noble gases occur as minor constituents of the atmosphere (about 1%). The electronic configurations and some physical properties of noble gases are given in the Table 5.5.

**Table 5.5 Electronic Configurations and Physical Properties of Noble Gases**

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Electronic configurations	$1s^2$	(He) $2s^2 2p^6$	(Ne) $3s^2 3p^6$	(Ar) $3d^{10} 4s^2 4p^6$	(Kr) $4d^{10} 5s^2 5p^6$	(Xe) $5d^{10} 6s^2 6p^6$
Ionization energy ( $\text{kJmol}^{-1}$ )	2372	2080	1520	1351	1170	1037
Atomic radius (pm)	31	71	98	112	131	140
Melting points ( $^{\circ}\text{C}$ )	-246	-249	-189	-157	-112	-71
Boiling points ( $^{\circ}\text{C}$ )	-269	-246	-186	-153	-108	-62
Water solubility (ml/lit) at $20^{\circ}\text{C}$	13.8	14.7	37.9	73.00	110.9	
Heat of vapourization ( $\text{kJmol}^{-1}$ )	0.08	1.77	6.5	9.7	13.7	18.0



The noble gases are isolated from air, either by fractional distillation or by some chemical method. The principal commercial source of Ne, Ar, Kr and Xe is air.

Helium is present on earth as a result of radioactive decay. After hydrogen, it is the second most abundant element in the universe.  $\alpha$ -Particles are doubly ionized helium atoms  $\text{He}^{2+}$ . It is simple and economical to isolate the helium gas from certain natural gases by liquefaction method.

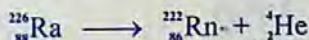
Argon is a colourless and odourless gas. It is very inert and not known to form any true chemical compound. It is obtained as a by-product during the liquefaction of air.

Neon is  $1/65000^{\text{th}}$  part of the atmosphere and it is also isolated during liquefaction of air. In a discharge tube, neon glows reddish (of all the noble gases, the discharge of neon is the most intense at ordinary voltage and current). Liquid neon has over 40 times more refrigeration capacity than liquid helium.

Traces of krypton are present in air. It is a colourless, odourless and fairly expensive gas. It is characterized by its brilliant green and orange spectral lines. Its compound krypton difluoride ( $\text{KrF}_2$ ) can be prepared by various methods.

Xenon is present in the atmosphere to a very small extent (0.08 ppm). It is obtained as a by-product during the fractional liquefaction of air. Xenon is available commercially in cylinders at high pressure. It reacts with fluorine but not with water. However it is slightly soluble in water to the extent of about 110 ml/lit at  $20^\circ\text{C}$ .

Radon is the  $\alpha$ -decay product of the radium. Radon is present to a very small extent in the atmosphere and it could be obtained as a by-product from the liquefaction of air. However, the small quantities of this gas which are usually needed can be collected from the radioactive decay of radium isotopes.



The noble gases have valence shells which are complete octets (except He). Due to complete shells their ionization energy values are very high. They have low boiling points. The boiling point of helium is the lowest of any known substance. Their boiling points increase with increasing atomic number down the group.

The very low values of melting and boiling points and low heats of vapourization show that noble gases have weak forces of attraction between their atoms. As there are no ordinary electron pair interaction, these weak forces must be of the van der Waals' type.

The solubility of the noble gases in water increases with increasing atomic number. This is because the bigger atoms are more readily polarized by water molecules.

### 5.7.2 Compounds of Xenon

Xenon reacts directly with fluorine only. The known oxidation state of Xenon in its compounds ranges from +2 to +8. These compounds are stable and can be obtained in large quantities. Some important compounds of Xenon are given in the Table 5.6.



Table 5.6 Compounds of Xenon

Oxidation state	Compound	Physical form	Melting Point (°C)
+2	XeF <sub>2</sub>	Colourless crystals	140
+4	XeF <sub>4</sub>	Colourless crystals	114
+4	XeOF <sub>2</sub>	Colourless crystals	90
+6	XeF <sub>6</sub>	Colourless crystals	48
+6	XeOF <sub>4</sub>	Colourless liquid	-28
+6	XeO <sub>3</sub>	Colourless crystals	25 (Explodes)
+8	XeO <sub>4</sub>	Colourless gas	-39.9 (Explodes, on warming)

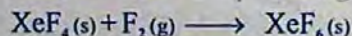
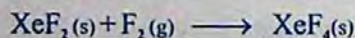
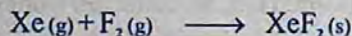
### 5.7.3 Fluorides of Xenon

Three known fluorides of Xenon are XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub>.

XeF<sub>2</sub> can be prepared by direct interaction of the elements. The compound formed should be removed immediately from the reaction zone, otherwise further reaction with F<sub>2</sub> will give XeF<sub>4</sub>. The reaction is completed in about 8 hours. XeF<sub>2</sub> is a crystalline solid. It is stored in nickel vessels. XeF<sub>2</sub> is a mild fluorinating agent.

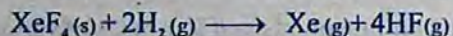
XeF<sub>4</sub> can be prepared by heating a mixture of Xe and F<sub>2</sub> in 1:5 ratio in a nickel container under 6 atmospheric pressure for a few hours. It can be stored in nickel vessels. Its properties are similar to that of XeF<sub>2</sub> but it is a strong fluorinating agent.

XeF<sub>6</sub> requires more severe conditions. Xe and F<sub>2</sub> are taken in 3:20 ratio in a stainless steel vessel and heated to 300°C at 50 atmospheric pressure. More than 95% conversion to XeF<sub>6</sub> takes place. XeF<sub>6</sub> is a crystalline solid. It is colourless in the solid state but yellow in liquid and gaseous forms.



#### Chemical Reactions

Fluorides of xenon can be reduced with hydrogen at 400°C, giving xenon and hydrofluoric acid.



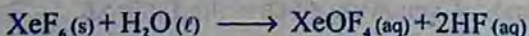
Xenon tetra-fluoride is a good fluorinating agent and can be used to prepare metal fluorides as follows:



Reaction occurs with explosion when XeF<sub>4</sub> is brought in contact with liquid ammonia.



Hydrolysis of XeF<sub>6</sub> with small amount of water gives XeOF<sub>4</sub>,





### 5.7.4 Xenon Oxyfluorides

Xenon oxytetrafluoride,  $\text{XeOF}_4$ , is also formed by a rapid reaction of  $\text{XeF}_6$  with silica (quartz).



$\text{XeOF}_4$  is a colourless volatile liquid. It can be kept in nickel vessel. It reacts with water to give  $\text{XeO}_3$ .



Xenon oxydifluoride,  $\text{XeOF}_2$ , is obtained when xenon reacts with oxygen difluoride in an electric discharge.



### 5.7.5 Oxides of Xenon

There are two oxides of xenon

1. Xenon trioxide
2. Xenon tetraoxide

#### 1. Xenon Trioxide $\text{XeO}_3$

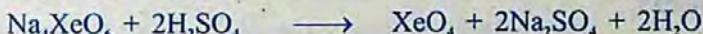
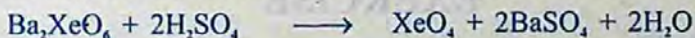
Xenon trioxide can be obtained when  $\text{XeF}_6$  is hydrolysed slowly.



It is a crystalline solid. It explodes at very low temperature. It is weakly acidic and its aqueous solution is almost non-conductor.

#### 2. Xenon Tetraoxide $\text{XeO}_4$

It is obtained by the addition of barium or sodium perxenate to conc.  $\text{H}_2\text{SO}_4$



### 5.7.6 Applications of the Noble Gases

1. Helium is used in weather balloons, in welding and in traffic signal lights.
2. A mixture of 80% helium and 20% oxygen is used for breathing by the sea divers.
3. Helium is used as a cooling medium for nuclear reactors.
4. Neon is largely used in making neon advertising signs, in high voltage indicators and TV tubes.
5. Neon and helium arc is used in making glass lasers.
6. Argon is used in electric light bulbs, in fluorescent tubes, in radio tubes, and in Geiger counters (used to detect radioactivity).
7. Argon is also used for arc welding and cutting.
8. Krypton is used to fill fluorescent tubes and in flash lamps for high speed photography.
9. Xenon is used in bactericidal lamps.
10. Radon being radioactive is used in radiotherapy for cancer and for earth quake prediction.



## KEY POINTS

1. The halogens are very reactive. Intermolecular forces in halogens increase down the group, fluorine is a gas but iodine is solid.
2. They form ionic compounds with s-block metals, covalent compounds with p-block elements and complex ions with d-block metals. Fluorides are usually ionic.
3. They show oxidation states -1, +1, +3, +5, +7 but fluorine shows the oxidation state of -1 only.
4. Oxidizing power of halogens decreases down the group in the following order:  

$$F_2 > Cl_2 > Br_2 > I_2$$
5. Reducing power of halide ions decreases from  $I^-$  to  $F^-$ . Chloride and fluoride ions are not reductants.
6. Chlorine, bromine and iodine form their respective oxides and oxyacids.
7. Halogens and their compounds are used for bleaching, refrigeration and as aerosols, etc.
8. Noble gases are placed in zero (VIII A) group of periodic table.
9. They have valence shells which are closed octets (except helium).
10. Very low values of melting and boiling points show that there are very weak forces of attraction between their atoms.
11. Oxides, fluorides and oxyfluorides of xenon can be prepared.
12. Noble gases have multi-dimensional uses.

## EXERCISE

Q.1 Fill in the blanks.

- (i) The halogen with the highest electronegativity is \_\_\_\_\_.
- (ii) HI is \_\_\_\_\_ agent.
- (iii) The only halogen acid which is not a strong acid is \_\_\_\_\_.
- (iv) Tincture of \_\_\_\_\_ is a common antiseptic.
- (v) The halogen with the lowest melting and boiling points is \_\_\_\_\_.
- (vi) Bleaching powder is prepared from \_\_\_\_\_ and \_\_\_\_\_.
- (v) \_\_\_\_\_ is the halogen which causes burns on the skin which heal slowly.
- (viii) \_\_\_\_\_ is used for making unshrinkable wool.
- (ix) A mixture of \_\_\_\_\_ and \_\_\_\_\_ is used for breathing by the sea divers.
- (x) Noble gas used to fill fluorescent tubes is \_\_\_\_\_.

Q.2 Indicate True or False.

- (i) HF is used for etching glass.
- (ii) HI is weaker reducing agent as compared to HF.



- (iii) Bleaching powder is completely soluble in water.
- (iv) The formula of perchloric acid is  $\text{HClO}_4$ .
- (v) On warming, aqueous  $\text{KOC1}$  disproportionates as follows.  
$$3\text{KOC1} \rightarrow 2\text{KCl} + \text{KClO}_3$$
- (vi)  $\alpha$ -particles emitted by radioactive elements are ions of radon.
- (vii) Radon is the only one of the noble gases that is radioactive.
- (viii) The molecules of the noble gases are all monoatomic.
- (ix) Argon is used to fill electric bulbs.
- (x) The noble gas which is present in the largest amount in atmosphere is krypton.

Q 3. Multiple choice questions. Encircle the correct answer.

- (i) Which of the following hydrogen halide is the weakest acid in solution?  
(a) HF (b) HBr (c) HI (d) HCl
- (ii) Chlorine heptaoxide ( $\text{Cl}_2\text{O}_7$ ) reacts with water to form:  
(a) Hypochlorous acid (b) Chloric acid  
(c) Perchloric acid (d) Chlorine and oxygen
- (iii) Hydrogen bond is the strongest between the molecules of:  
(a) HF (b) HCl (c) HBr (d) HI
- (iv) Which halogen will react spontaneously with  $\text{Au(s)}$  to produce  $\text{Au}^{3+}$ ?  
(a)  $\text{Br}_2$  (b)  $\text{F}_2$  (c)  $\text{I}_2$  (d)  $\text{Cl}_2$
- (v) The anhydride of  $\text{HClO}_4$  is:  
(a)  $\text{ClO}_3$  (b)  $\text{ClO}_2$  (c)  $\text{Cl}_2\text{O}_5$  (d)  $\text{Cl}_2\text{O}_7$
- (vi) Bleaching powder may be produced by passing chlorine over:  
(a) calcium carbonate (b) hydrated calcium sulphate  
(c) anhydrous calcium sulphate (d) calcium hydroxide  
(e) magnesium hydroxide
- (vii) Which is the strongest acid?  
(a)  $\text{HClO}$  (b)  $\text{HClO}_2$  (c)  $\text{HClO}_3$  (d)  $\text{HClO}_4$
- (viii) Which halogen occurs naturally in a positive oxidation state?  
(a) Fluorine (b) Chlorine (c) Bromine (d) Iodine
- (ix) An element that has a high ionization energy and tends to be chemically inactive would most likely to be:  
(a) an alkali metal (b) a transition element  
(c) a noble gas (d) a halogen
- (x) Which of the following represents the correct electronic configuration of the



outermost energy level of an element of zero (VIII A) group in the ground state.

- (a)  $s^2p^2$  (b)  $s^2p^4$  (c)  $s^2p^5$  (d)  $s^2p^6$

- Q.4 What is bleaching powder? How is it prepared commercially? Give its uses.
- Q.5 (a) Discuss the oxides of chlorine.  
(b) What are disproportionation reactions? Explain your answer with an example.
- Q.6 Discuss the system of nomenclature used for oxyacid of halogens. Support your answer with examples.
- Q.7 (a) How the halogen acids are ionized in water?  
(b) Why HF is weaker acid than HCl?
- Q.8 In the following sets, arrange the substances in order of the property indicated. Give reasons.  
(a) Increasing acidic character  
 $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$   
(b) Increasing oxidizing power  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ .
- Q.9 What happens when bleaching powder reacts with the following reagents dil.  $\text{H}_2\text{SO}_4$ , excess of cone.  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$ ,  $\text{HI}$  and  $\text{CO}_2$ .
- Q.10 Discuss the various commercial uses of halogens and their compounds.
- Q.11 What are noble gases? Explain their inertness on the basis of their electronic configuration.
- Q.12 Write notes on the followings.  
(i) Oxyfluorides of xenon.  
(ii) Applications of noble gases.
- Q.13 Short questions.  
(i) What is "Iodized Salt"?  
(ii) What are Freons and Teflon?  
(iii) Arrange the following ions in order of increasing size:  
 $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$   
(iv) Why iodine has metallic luster?  
(v) Which halogen sublimes to violet vapours?  
(vi) Which halogen is used as an antiseptic?  
(vii) Which halogen is used in water treatment to kill bacteria?  
(viii) Name the gas, which is used for earthquake prediction.  
(ix) Name the gas, which is used in bactericidal lamps.