

# UNIT 10 ELEMENTS OF GROUP 17

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## 10.1 INTRODUCTION

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In Unit 1 you studied the periodic table which gives the classification of elements into various periods and groups. You have seen that in any period the element in Group 1 is the most electropositive and metallic in nature. As we go across a period from Group 1 to Group 17 of the main group elements, nonmetallic nature, ionisation energy, electron affinity and electronegativity increase, reaching a maximum at Group 17. In this way, at one extreme we have Group 1 comprising alkali metals and at the other we have Group 17 comprising non-metals, namely, fluorine, chlorine, bromine, iodine and astatine, collectively called the **halogens**. Halogens derive their name from the Greek words, halos + gens meaning salt producers, as they form salts in combination with metals. The most common of the salts being sodium chloride or the common salt. Halogens find a wide variety of uses in everyday life. In view of their nature and usefulness, it will be interesting to study the chemistry of halogens.

### Objectives

After studying this unit, you should be able to:

- explain the occurrence, extraction and uses of halogens,
  - describe the isolation of fluorine,
  - list the general characteristics of halogens and describe their reactions,
  - describe the chemistry of hydrogen halides, halogen oxides and oxoacids,
  - describe the chemistry and geometry of interhalogen compounds and polyhalides, and
  - explain the anomalous behaviour of fluorine.
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## 10.2 OCCURRENCE, EXTRACTION AND USES

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Chemistry of halogens is very interesting and has varied applications in our daily life. Due to their high reactivity, halogens do not occur free in nature. In the combined form, however, they are fairly abundant. In this section you will study their occurrence, extraction and some important uses.

### 10.2.1 Occurrence

Fluorine is the first element of this group; it constitutes nearly 0.054% of earth's crust, where it occurs as fluor spar ( $\text{CaF}_2$ ), cryolite ( $\text{AlF}_3 \cdot 3\text{NaF}$ ) and fluorapatite [ $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$ ].

Small amounts of fluorides occur in sea water and in some mineral springs. Bones also contain small amounts of fluorine. A six mile long belt of fluorspar has been recently discovered in Dungarpur (Rajasthan) and is considered to be sufficient to meet the needs of the country.

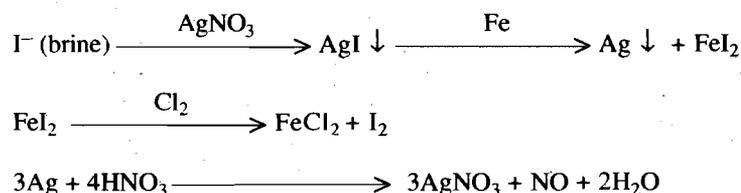
Chlorine, which forms 0.013% of earth's crust, occurs mainly as chlorides of sodium and other alkali and alkaline earth metals in salt mines as well as in sea water. Sea water is almost a 3% solution of various salts, of which sodium chloride forms ~83%. Bromine, as bromides, occurs in sea water and dry salt lakes and constitutes about  $2.0 \times 10^{-4}\%$  of earth's crust. Iodine is the rarest of all the halogens, forming only  $4.6 \times 10^{-5}\%$  of earth's crust. Its main source used to be **kelp**, or the ash obtained on burning sea weeds, and **Chile saltpetre** in which it occurs as iodates. However, now it is mostly extracted from brine. Astatine is a radioactive element. The naturally occurring isotopes of astatine have half-lives of less than one minute. Therefore, it occurs in negligible amounts in nature. The isotope  $^{211}_{85}\text{At}$  At having the longest half-life of 7.21 hours, is made by bombarding bismuth with  $\alpha$  particles.



### 10.2.2 Extraction

The only practicable method of preparing fluorine gas is Moissan's original procedure based on the electrolysis of KF dissolved in anhydrous HF. The details of this method along with some other methods for the isolation of fluorine have been given separately in Section 10.2.3. You have already studied in Unit 3 that chlorine is obtained as a byproduct along with hydrogen in the manufacture of sodium hydroxide by electrolysis of brine. Electrolysis of molten sodium chloride also gives chlorine and sodium. In some parts of the world, it is produced by the electrolysis of aqueous HCl. Bromine is made on an industrial scale by reaction of bromides with chlorine. A mixture of air and chlorine is blown through an aqueous solution of a bromide at a pH of 3.5. Chlorine displaces bromine and air blows it out of the solution.

Iodine can also be prepared similarly by the oxidation of iodides by chlorine. Iodine is also prepared by treating brine with  $\text{AgNO}_3$  to precipitate  $\text{AgI}$ . This is possible because  $\text{AgI}$  is the least soluble of all the silver halides. Precipitated  $\text{AgI}$  is treated with clean scrap iron or steel to form metallic silver and a solution of  $\text{FeI}_2$ . This solution is then treated with chlorine to liberate  $\text{I}_2$ . Precipitated silver is redissolved in dil.  $\text{HNO}_3$  to give  $\text{AgNO}_3$  which is used again to precipitate  $\text{AgI}$ .



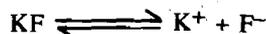
### 10.2.3 Preparation of Fluorine

Isolation of fluorine presented a tough problem to chemists for about a century. Though its existence was first shown by Davy in 1813, yet it could not be isolated before 1886. All attempts at isolation of fluorine failed due to the following reasons :

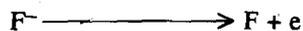
- High chemical reactivity of fluorine towards other elements.
- It attacked the apparatus whether made of glass, carbon, platinum or any other metal in which its preparation was tried.
- In view of fluorine being the most powerful oxidant, no oxidising agent could be available which could bring about the oxidation of HF to  $\text{F}_2$ . Therefore, the only method available was that of electrolysis.
- The method of electrolysis was not fruitful. Aqueous HF on electrolysis yields hydrogen and oxygen. On the other hand anhydrous HF was found to be a non-conductor of electricity.

- v) Exceedingly poisonous and corrosive character of anhydrous HF proved fatal to early chemists.

All the above mentioned reasons were very disheartening. However, Moissan picked up courage and entered this field. He electrolysed a cooled solution of KF in anhydrous liquid HF at 250 K using platinum-iridium electrodes sealed with fluorspar caps in a platinum U-tube. In this reaction, the actual electrolyte is KF while HF acts as an ionising solvent,  $F_2$  is evolved at the anode and  $H_2$  at the cathode as indicated below :



At the anode



At the cathode



Potassium fluoride thus formed again undergoes electrolysis. As the hydrogen fluoride is used up, more is added to prevent the melting point of the mixture from rising. The outgoing gases,  $F_2$  and  $H_2$ , are not allowed to mix up in the electrolytic cell. The fluorine gas is collected in plastic receivers.

Moissan's original method has been modified. In place of the expensive Pt/Ir alloy, cells made of copper, steel or Monel metal, which is a nickel-copper alloy, have been used. These get covered by a thin protective film of the fluoride just as aluminium is protected by the thin film of oxide. Anode is a carbon rod impregnated with copper to render it inert and cathode is made of steel or copper. A mixture of KF and HF in the molar ratio of 1:1 or 1:2 is used as electrolyte giving a working temperature of 515 K or 345 K, respectively.

### 10.2.4 Uses

The main use of halogens is in the halogenation of organic and inorganic compounds. You must have heard of or used the tincture of iodine (iodine dissolved in alcohol) as an antiseptic. Iodine is present in the thyroid hormone. A deficiency of iodine causes goitre and leads to stunted growth and cretinism. To prevent this, common salt is routinely iodised. You must have used toothpastes containing fluorides in order to prevent tooth decay by dental caries. You are aware that naturally occurring uranium is a mixture of two isotopes –  $^{238}\text{U}$  (99.3%) and  $^{235}\text{U}$  (0.7%). Of the two, the latter is fissionable and is used for the generation of nuclear power. Fluorine is used for the production of uranium hexafluoride, the compound used for separation of  $^{235}\text{U}$  and  $^{238}\text{U}$  isotopes by gaseous diffusion method. Besides this, liquid fluorine was used as an oxidant in rocket fuels but this has now been discontinued. Teflon, so familiar to modern housewife in the form of its coating on kitchenware to make them nonsticking, is a polymer of fully fluorinated ethylene. You have already studied in Unit 7, the use of chlorofluorocarbons or CFCs as refrigerants, in aerosol sprays and in micro-electronics. Freons, e.g.,  $\text{CCl}_2\text{F}_2$  (Freon-12) and  $\text{CCl}_3\text{F}$  (Freon-11) used as refrigerants also contain fluorine. Bleaching powder,  $\text{CaOCl}_2$ , is used for bleaching paper pulp and textiles. Bleaching powder or liquid chlorine is used for disinfection of water on a large scale. Chlorine was used in the chemical warfare in World War I. The most important use of chlorine is in the manufacture of polyvinylchloride or PVC, which because of its non-inflammability and insulating properties is used as an electrical insulator, for covering electric wires, making conduit pipes, etc. Dichlorodiphenyltrichloroethane (DDT) is used widely as an insecticide. Methyl bromide is the most effective nematocide known. It is also used as a general pesticide. The use of silver bromide in making photographic plates or films is a common knowledge.

### SAQ 1

Why can't fluorine be obtained by electrolysis of an aqueous solution of NaF ?

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## 10.3 GENERAL CHARACTERISTICS

All elements of Group 17 have seven electrons in their outermost shell, with configuration  $ns^2, np^5$ . Thus, they are just one electron short of the electronic configuration of noble gases. The single unpaired electron in  $p$ -orbital is responsible for chemical bonding with other elements. Let us now discuss some of their physical and chemical properties.

### 10.3.1 Physical Properties

Halogens exist as non-polar diatomic molecules which are coloured. Fluorine is pale yellow, chlorine is yellowish green, bromine is brown and iodine is violet in the gaseous state. Solid iodine is almost black with a shiny metallic lustre. Except iodine which has some useful biological applications, halogens are very hazardous and toxic, fluorine being the most. Their vapours produce a choking sensation when inhaled.

Some of the physical properties of the halogens are listed in Table 10.1

Table 10.1: Some physical properties of halogens

Property	Fluorine F	Chlorine Cl	Bromine Br	Iodine I
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>
Atomic weight	18.9984	35.453	79.909	126.904
Density (liquid) (10 <sup>3</sup> × kg m <sup>-3</sup> )	1.11	1.56	3.17	4.94
Ionic radius X <sup>-</sup> (pm)	136	181	195	216
Covalent radius (pm)	64	99	114	133
Melting point (K)	53	172	266	386
Boiling point (K)	85	238.5	332	456
Enthalpy of fusion (kJ mol <sup>-1</sup> )	0.26	3.2	5.27	7.8
Enthalpy of vaporisation (kJ mol <sup>-1</sup> )	3.27	10.2	15	30
Enthalpy of atomisation (kJ mol <sup>-1</sup> )	79.1	122	111	106
Enthalpy of hydration X <sup>-</sup> (g) (kJ mol <sup>-1</sup> )	460	385	351	305
Electronegativity (A/R)	4.10	2.85	2.75	2.20
Ionisation energy (kJ mol <sup>-1</sup> )	1681	1255	1142	1007
Electron affinity (kJ mol <sup>-1</sup> )	333	348	340	297
Electrode potential 1/2X <sub>2</sub> (g) + e <sup>-</sup> → X <sup>-</sup> (aq)	+2.87	+1.36	+1.07	+0.54
Oxidation states	-1	-1, I, III, V, VII	-1, I, III, V	-1, I, III, V, VII
Lattice energy (kJ mol <sup>-1</sup> ) (Potassium salt)	817	718	656	615
Bond dissociation energy (X-X) (kJ mol <sup>-1</sup> )	158	244	192	152

Physical properties like melting and boiling points are related to the size and mass of the molecules as well as intermolecular attraction. The effect of size and mass, which gradually increase as we go down the group, is easy to understand. As for the intermolecular attraction in non-polar homonuclear diatomic molecules like halogens, which do not have any permanent polarity, the only forces of attraction are the weak van der Waals forces. The polarisability of halogens increases as we go down the group, begin maximum in iodine and least in fluorine. So, van der Waals forces of attraction are maximum in iodine and least in fluorine, with bromine and chlorine coming in between. As a consequence of this, fluorine and chlorine are gases at ordinary temperature, bromine is a liquid and iodine a solid. This is also reflected in the trends observed in their enthalpies of fusion and vaporisation (Table 10.1).

You have already learnt in Unit 2 that as we move along a period, the effective nuclear charge increases reaching a maximum at the noble gases. Halogens which immediately precede the noble gases have a very high effective nuclear charge coupled with small size and thus have the highest ionisation energies in the respective periods, next only to the noble gases. Like the trend in other groups, ionisation energy of halogens also decreases in going down the group from fluorine to iodine.

Halogens have seven electrons in their valence shell, they have a very strong tendency of gaining an electron to acquire a stable noble gas configuration. Therefore, they have very high electron affinities. In fact, their electron affinities are the highest in their respective

periods. Their electron affinity follows the order  $\text{Cl} > \text{F} > \text{Br} > \text{I}$ . As explained in Unit 2, the smaller electron affinity of fluorine than that of chlorine is a consequence of its small size.

You know that as we go across the  $p$ -block elements in a period, the electronegativity increases reaching a maximum at the halogen group. Thus, halogens are the most electronegative elements in their respective periods. Electronegativity decreases on moving down a group, making fluorine the most and iodine the least electronegative among the halogens.

In going down the group from chlorine to iodine, the X-X bond dissociation energy gradually decreases (Table 10.1). This is easily explained by considering once again the size factor. In the chlorine molecule, which is the smallest of the three, viz.,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ , the two bonding electrons are nearer to both the nuclei and are held strongly, while in bromine and iodine, the distance of the bonding electrons from the nuclei gradually increases resulting in lesser attraction and consequent weakening of the bond. Furthermore, as the size of the atom increases, it results in a less effective overlap of the orbitals and therefore, progressively weaker bonds are formed as we go down the group. The bond dissociation energy increases in the order  $\text{I}_2 < \text{Br}_2 < \text{Cl}_2$  and if this trend was to continue, you should expect the F-F bond dissociation energy to be greater than the bond energy of chlorine,  $244 \text{ kJ mol}^{-1}$ . But this is not so. The actual bond dissociation energy of fluorine molecule is, however, surprisingly low and has the value of  $158 \text{ kJ mol}^{-1}$  only. The anomalously low bond dissociation energy of fluorine molecule is attributed to the fact that fluorine atom is very small and the non-bonding electrons on fluorine are nearer to each other, resulting in a much greater lone pair-lone pair repulsion, which weakens the covalent bond and lowers its dissociation energy. This repulsion is not so great in relatively larger halogen molecules like chlorine, bromine and iodine where the lone pairs are at a greater average distance from each other.

### SAQ 2

Fill the name of the appropriate halogen in the space provided against each of the following:

Which of the halogens

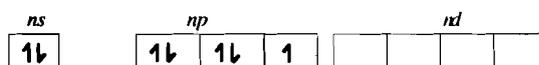
- i) has two complete electron shells  
below the valence shell .....
- ii) is solid at room temperature .....
- iii) has highest electronegativity value .....
- iv) lowest ionisation energy .....

### 10.3.2 Oxidation States

Fluorine is always univalent. Since it is the most electronegative element, it always has the oxidation number  $-1$ . Fluorine has no  $d$ -orbital in its valence shell, hence it cannot have any excited states or any other oxidation number.

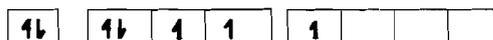
Oxidation state of  $-1$  is the most common and stable one for other halogens also. However, consistent with the decreasing electronegativity,  $-1$  oxidation state becomes gradually less stable in going down the group. As chlorine, bromine and iodine are less electronegative than fluorine and oxygen, they exhibit an oxidation state of  $+1$  in their fluorides and oxides. In addition, except fluorine all the other halogens exhibit oxidation states of  $+3$ ,  $+5$  and  $+7$  due to the availability of vacant  $d$ -orbitals as shown below:

Halogen (except F)  
atom in ground state



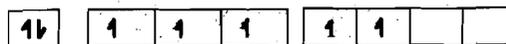
Oxidation state =  $\pm 1$ ,  
e.g., HCl, HBr & HI  
(oxidation =  $-1$ ),  
HClO, HBrO & HIO  
(oxidation state =  $+1$ )

Halogen atom in  
1st excited state



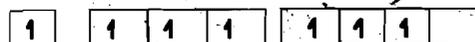
oxidation state =  $+3$ ,  
e.g.,  $\text{ClF}_3$ ,  $\text{BrF}_3$

Halogen atom in the  
2nd excited state



oxidation state = +5,  
e.g.,  $\text{HClO}_3$ ,  $\text{HBrO}_3$ ,  $\text{HIO}_3$

Halogen atom in the  
3rd excited state

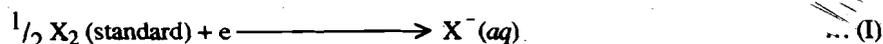


oxidation state = +7  
e.g.,  $\text{HClO}_4$ ,  $\text{HIO}_4$

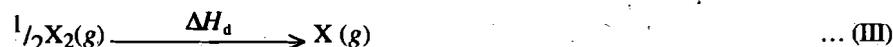
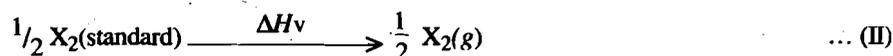
Chlorine and bromine also exhibit oxidation state +4 ( $\text{ClO}_2$  and  $\text{BrO}_2$ ) and +6 ( $\text{Cl}_2\text{O}_6$  and  $\text{Br}_2\text{O}_6$ ). Iodine exhibits an oxidation state +4 in  $\text{I}_2\text{O}_4$ .

### 10.3.3 Oxidising Power

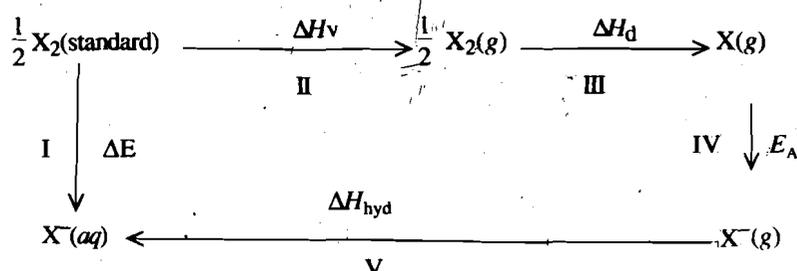
Oxidation may be regarded as the removal of electrons, so that the oxidising agent gains electrons. Since halogens have a greater tendency to pick up electrons, they act as strong oxidising agents. Their oxidising power, however, decreases on moving down the group. The strength of an oxidising agent or its ability to accept electrons, depends on several energy terms. The reaction,



representing the oxidising action of a halogen, is actually a complicated process. It involves the following steps:



The above changes are represented in the form of Born-Haber cycle, as shown below :



Evidently, since energy is invariably absorbed in steps (II) and (III), enthalpy of vapourisation,  $\Delta H_v$  and enthalpy of dissociation,  $\Delta H_d$ , always have positive values. However, energy is released in steps (IV) and (V), hence, electron affinity,  $E_A$ , and enthalpy of hydration,  $\Delta H_{\text{hyd}}$  are negative. Consequently, from Hess's law, the net enthalpy change,  $\Delta E$  for the reduction reaction (I) is given by the expression:

$$\Delta E = \Delta H_v + \Delta H_d + E_A + \Delta H_{\text{hyd}}$$

#### Hess's Law:

The amount of heat evolved in a chemical process is always the same irrespective of whether the process goes as a one or many step reaction.

For fluorine and chlorine which are gases at room temperature, the enthalpy of evaporation is omitted. Enthalpy changes associated with each of the above steps and the net enthalpy change,  $\Delta E$  are given in Table 10.2.

You can see from Table 10.2 that  $\Delta E$ , or the net enthalpy change associated with the reaction (I) decreases from fluorine to iodine. Considering that the difference in entropy changes are small and mainly enthalpy changes determine the free energy change, it can be inferred that the free energy change for reaction (I) becomes less negative on descending the group. In other words, fluorine is the strongest oxidising agent of the four. Thus, you may note that despite the electron affinity of chlorine being highest, fluorine is the strongest oxidising agent because of its low enthalpy of dissociation and high enthalpy of hydration.

Thus, it is the total enthalpy change and not the electron affinity which controls the strength of an oxidising agent.

Table 10.2 : Enthalpy values for  $\frac{1}{2} X_2 \longrightarrow X^-(aq)$

Molecule	Enthalpy of vapourisation, $\Delta H_v$ kJ mol <sup>-1</sup>	Enthalpy of dissociation, $\Delta H_d$ kJ mol <sup>-1</sup>	Electron affinity, $E_A$ kJ mol <sup>-1</sup>	Enthalpy of hydration, $\Delta H_{hyd}$ kJ mol <sup>-1</sup>	$\Delta E$ kJ mol <sup>-1</sup>
F <sub>2</sub>	—	+79.2	-333	-460	-714
Cl <sub>2</sub>	—	122.0	-348	-385	-611
Br <sub>2</sub>	15	96.0	-340	-351	-580
I <sub>2</sub>	30	76.0	-297	-305	-496

The oxidising power of the halogens in the solid state reactions also shows the same order. This is because lattice energies of the ionic halides (Table 10.1) follow the same order as the hydration energy; fluorides having the highest and iodides the lowest lattice energy.

Another important factor which makes fluorine the strongest oxidising agent is the high element-fluorine covalent bond energy as shown in Table 10.3.

Table 10.3 : Halogen-element bond energy, kJ mol<sup>-1</sup>

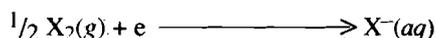
Element	B	C	N	O	F	Si	P	S	Cl	H
F	644	489	286	213	158	598	498	285	251	565
Cl	433	326	192	205	251	402	331	272	244	431
Br	368	272		201	251	331	268	213	209	364
I	272	238			243	234	184		209	299

You will notice that the values in the first row representing fluorine-element bond energy are highest except in the case of fluorine-fluorine bond energy; the reasons for which you have studied earlier in Section 10.3. Thus fluorine forms a very strong bond with almost all other elements. A consequence of this is that fluorine is able to form compounds with other elements in their higher oxidation states. The order of the ability of the halogens to combine with elements in higher oxidation states is F > Cl > Br > I.

A comparison of the reduction potential of halogens with that of oxygen can indicate which of them would oxidise water to oxygen. The standard electrode potential for reduction of oxygen to water in acid solution is 1.23 volts:



The standard reduction potential of the halogen half cell reaction,



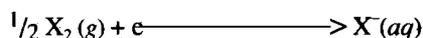
is +2.87 volts in the case of fluorine and +1.36 volts in the case of chlorine (Table 10.1). These are more positive than that for reduction of oxygen to water. These two halogens can, therefore, oxidise water to oxygen. Fluorine does so readily but chlorine reacts rather slowly, at first giving HClO which later decomposes to oxygen and HCl. The electrode potentials of bromine and iodine are less than that of oxygen, therefore, they are not able to oxidise water to oxygen.

To sum up, the main thermodynamic factors responsible for making fluorine so uniquely highly oxidising and reactive are:

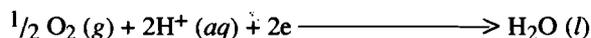
- high hydration energy of the fluoride ion
- high lattice energy of ionic fluorides
- low F-F bond energy and
- high element fluorine bond energy.

## SAQ 3

Table 10.1 lists the standard reduction potential for the half cell reaction,



and the standard potential for the reaction



is 1.23V. What reaction do you predict between bromine and water and iodine and water on this basis?

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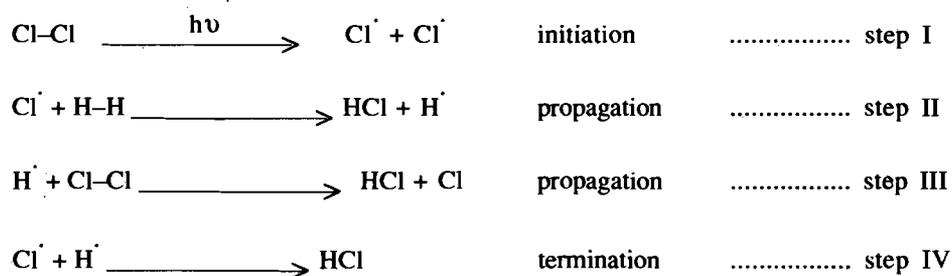
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### 10.3.4 Chemical Properties

All the halogens are very reactive. Fluorine is the most reactive of all the halogens, combining directly with every other element except oxygen and some of the noble gases. Therefore, it is also called a **super halogen**. You have also seen that the reactivity decreases from  $F_2$  to  $I_2$ . In displacement reactions we find that fluorine displaces all the remaining three halogens from their salts, chlorine displaces bromine and iodine and bromine displaces only iodine. Halogens react with each other to form **interhalogen compounds**, brief description of these is given in Section 10.4.4. Halogens, in general, react with most metals, though bromine and iodine do not react with some noble metals like Ag, Au. Halogens also react with many non-metals to form halides.

Halogens react with hydrogen to form hydrides which are called hydrogen halides. Fluorine and chlorine react with hydrogen with explosive violence, fluorine-hydrogen mixture explodes even in the dark. Chlorine-hydrogen mixture does so only in presence of light. This is called a **photochemical reaction**. It has been shown that this reaction starts with the formation of halogen free radicals. It is not surprising in view of the lower X-X bond energy as compared to H-H bond energy. Reactions of bromine and iodine with hydrogen are slow, the latter being reversible.

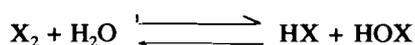


Such reactions are called **Chain Reactions** since after the initiation of the reaction, the propagation steps II and III are repeated in sequence till the reactants are consumed. The reaction gets terminated when free radicals start combining with each other as in step IV.

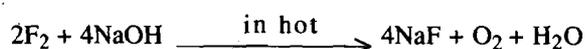
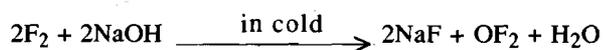
Fluorine reacts vigorously with water to form hydrofluoric acid and oxygen :



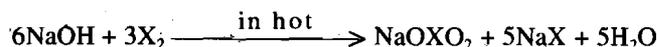
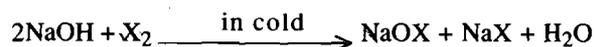
The other halogens are sparingly soluble in water ( $Br_2 > Cl_2 > I_2$ ) and react partly to give a mixture of hydrohalic and hypohalous acids :



Halogens react with aqueous alkali, the reactivity decreasing from fluorine to iodine. Fluorine behaves differently from other halogens. It reacts with alkalis violently forming fluorides and fluorine oxides or oxygen as shown below :



Other halogens react with alkalis in cold to give hypohalites ( $XO^-$ ) and in hot to form halates ( $XO_3^-$ ):



(where X = Cl, Br or I)

All halogens react with hydrocarbons but reactivity decreases with the increase in atomic number. Fluorine is the most reactive and brings about decomposition of the hydrocarbons:



Chlorine and bromine substitute hydrogen atoms, reaction with bromine being slower. Iodine has little or no reaction:



Some more reactions of halogens are summarised in Table 10.4.

Table 10.4: Some reactions of halogens

General Reaction	Remarks
$nX_2 + 2M \longrightarrow 2MX_n$	$F_2, Cl_2$ with practically all metals; $Br_2, I_2$ with all except noble metals.
$X_2 + H_2 \longrightarrow 2HX$	Reaction with iodine reversible.
$3X_2 + 2P \longrightarrow 2PX_3$	Similar reactions with As, Sb, Bi.
$5X_2 + 2P \longrightarrow 2PX_5$	With excess $X_2$ , but not with $I_2$ ; $SbF_5, SbCl_5, AsF_5, AsCl_5$ and $BiF_5$ may be prepared similarly.
$X_2 + 2S \longrightarrow S_2X_2$	With $Cl_2, Br_2$ .
$X_2 + H_2O \longrightarrow H^+ + X^- + HOX$	Not with $F_2$ .
$2X_2 + 2H_2O \longrightarrow 4H^+ + 4X^- + O_2$	$F_2$ rapidly, $Cl_2$ and $Br_2$ slowly in sunlight.
$X_2 + H_2S \longrightarrow 2HX + S$	
$X_2 + CO \longrightarrow COX_2$	$X_2 = Cl_2, Br_2$ .
$X_2 + SO_2 \longrightarrow SO_2X_2$	$X_2 = F_2, Cl_2$ .
$X_2 + Y_2 \longrightarrow 2XY$	Formation of interhalogen compounds (all except IF).

[X and Y are two different halogens]

### 10.3.5 Basic Properties of Halogens

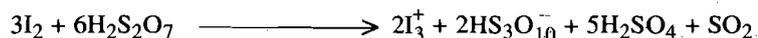
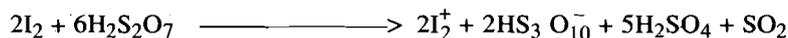
In general, the basic or metallic nature of elements increases as we descend down a group. Thus, you have seen in preceding units that the last member of each of the Groups 14, 15 and 16, i.e., Pb, Bi and Po, respectively, is definitely metallic in character. But, this trend is not so well marked in the elements of Group 17 because very little is known about the last member of the group, astatine. There is, however, definite evidence to show the existence of halogen cations in media which are weakly nucleophilic.

Fluorine is the most electronegative element and has no basic properties. Chlorine shows a slight tendency to form cations. For example,  $ClF$  ionises to form  $Cl^+$  and  $F^-$  due to the

Hypohalites are oxidising agents. Bleaching powder  $CaCl(OCl)$  owes its bleaching action to its oxidising properties.

higher electronegativity of fluorine. Bromine cation,  $\text{Br}^+$ , exists in complexes such as  $[\text{Br}(\text{pyridine})]^+ \text{NO}_3^-$ . Electrolysis of  $\text{ICN}$  in pyridine solution gives iodine at the cathode. This indicates that  $\text{ICN}$  ionises to  $\text{I}^+$  and  $\text{CN}^-$ . Many pyridine complexes, e.g.,  $[\text{I}(\text{pyridine})]^+ \text{NO}_3^-$ ,  $[\text{I}(\text{pyridine})_2]^+ \text{ClO}_4^-$  and  $[\text{I}(\text{pyridine})\text{CH}_3\text{COO}]^+$  containing  $\text{I}^+$  are known.

Iodine dissolves in oleum giving a bright blue solution which has been shown to have  $\text{I}_2^+$  and  $\text{I}_3^+$ :



Electrical conductivity of molten iodine is due to the presence of  $\text{I}_3^+$  +  $\text{I}_3^-$  species produced by the self ionisation of iodine:



The cations,  $\text{Cl}_3^+$  and  $\text{Br}_3^+$  are formed in the following reactions:



#### SAQ 4

Complete the following reactions:

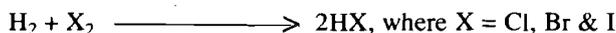
- i)  $\text{I}_2 + \text{IF}_3 \longrightarrow \dots\dots\dots$
- ii)  $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \dots\dots\dots + \dots\dots\dots$
- iii)  $\text{Cl} + 2\text{NaOH} \longrightarrow \dots\dots\dots + \dots\dots\dots + \dots\dots\dots$
- iv)  $\text{Cl}_2 + \text{H}_2\text{S} \longrightarrow \dots\dots\dots + \dots\dots\dots$
- v)  $\text{CH}_4 + 4\text{Br}_2 \longrightarrow \dots\dots\dots + \dots\dots\dots$

## 10.4 COMPOUNDS OF HALOGENS

In the preceding section you have learnt that the halogens form a variety of compounds with other elements. In this section, you will study the salient features of the chemistry of some of these compounds, viz., hydrogen halides, halogen oxides, oxoacids of halogens and the interhalogen compounds.

### 10.4.1 Hydrogen Halides

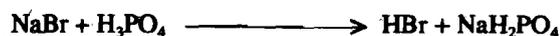
You have studied in the preceding section that all the halogens combine with hydrogen and form volatile hydrides of the type  $\text{HX}$ , which are also known as hydrogen halides. The reaction of fluorine with hydrogen is very violent whereas bromine and iodine react with hydrogen only at elevated temperatures and in the case of iodine the reaction does not proceed to completion:



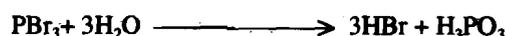
Hydrogen fluoride and hydrogen chloride are obtained by the action of concentrated sulphuric acid on fluorides and chlorides:



Since concentrated sulphuric acid partially oxidises  $\text{HBr}$  and  $\text{HI}$  to  $\text{Br}_2$  and  $\text{I}_2$ , these are prepared by the action of concentrated orthophosphoric acid on bromides and iodides:



Hydrogen bromide and hydrogen iodide are usually prepared in the laboratory by the hydrolysis of  $\text{PBr}_3$  and  $\text{PI}_3$ :



Under ordinary conditions  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{HI}$  are gases while  $\text{HF}$  is a liquid, due to strong hydrogen bonding. Their melting and boiling points show a gradual increase in the order  $\text{HCl} < \text{HBr} < \text{HI}$ , but  $\text{H-F}$  does not follow the trend and has unexpectedly higher values. This is because of strong hydrogen bonding in  $\text{H-F}$  molecules about which you have studied in Unit 3. Due to hydrogen bonding  $\text{HF}_2^-$  ion is stable and gives salts like  $\text{KHF}_2$ .

Hydrogen halides are covalent compounds with varying degree of polarity of the  $\text{H-X}$  bond depending upon the electronegativity of the halogen atom. Thus,  $\text{H-F}$  bond is most polar and the decreasing order of polarity is  $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$  as shown by the per cent ionic character in these bonds.

Some physical properties of the hydrogen halides are listed in the Table 10.5.

Table 10.5: Physical properties of hydrogen halides

	Physical state	Colour	B.P. (K)	M.P. (K)	% dissociation at 373 K	Per cent ionic character
HF	liquid	Colourless	293	190	Very slight	44
HCl	gas	"	188	159	0.0014	17
HBr	gas	"	208	186	0.5	11
HI	gas	"	237	222	33	5

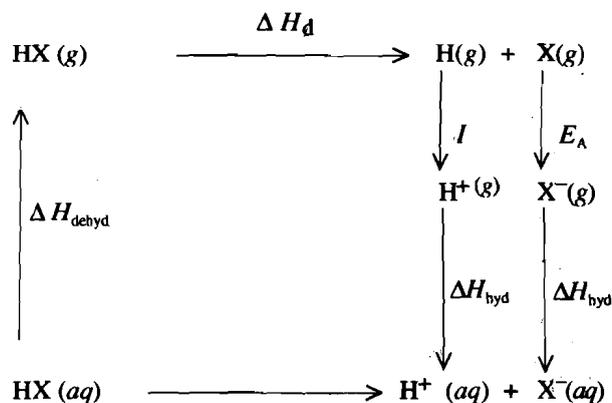
The thermal stability of hydrogen halides decreases from  $\text{HF}$  to  $\text{HI}$ . Thus hydrogen fluoride is the most stable whereas hydrogen iodide is the least stable. This can be seen from their percentage dissociation data (Table 10.5). For example, while  $\text{HF}$  and  $\text{HCl}$  are not appreciably dissociated even at 1473 K,  $\text{HBr}$  is dissociated to the extent of 0.5% and  $\text{HI}$  is dissociated to the extent of 33% at 373 K.

### Hydrohalic Acids

Aqueous solutions of hydrogen halides are called hydrohalic acids, viz., hydrofluoric, hydrochloric, hydrobromic and hydriodic acid. Hydrohalic acids form constant boiling point mixtures with water. The aqueous solutions of acids ionise as follows :



Their acid strength follows the order  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ . Acid strength is in general the tendency of  $\text{HX}(aq)$  to give  $\text{H}_3\text{O}^+(aq)$  and  $\text{X}^-(aq)$ . The enthalpy changes associated with the dissociation of hydrohalic acids can be represented with the help of Born-Haber cycle in its simplest form as given below:



A constant boiling point mixture is a mixture of two or more substances with a definite composition, which boils at a specific temperature at a specific pressure.  $\text{HCl}$ , for example forms a constant boiling point mixture containing 20.24%  $\text{HCl}$  with a boiling point 383 K.

The acid strength depends upon the sum of all enthalpy terms for various stages indicated in the Born Haber cycle. Of these the most marked change is in the enthalpy of dissociation of H-X bond, which decreases in the order HF > HCl > HBr > HI and the enthalpy of hydration of X<sup>-</sup>, which decreases from F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>. The total enthalpy change becomes more negative, i.e., the reaction,



becomes more exothermic from HF to HI. As expected, acid strength varies in the reverse order, HI being the strongest acid and HF the weakest acid.

### SAQ 5

Explain briefly in the space given below, why HF is the weakest acid.

.....

.....

.....

## 10.4.2 Halogen Oxides

All halogens form oxides. Numerous halogen oxides have been reported although many of them are unstable. These are listed in Table 10.6. Halogen-oxygen bonds are largely covalent because of the similarities in electronegativity of halogens and oxygen. Fluorine is more electronegative than oxygen, hence compounds of fluorine with oxygen are considered as fluorides of oxygen rather than oxides of fluorine.

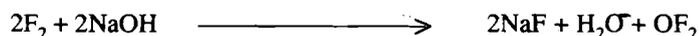
I<sub>2</sub>O<sub>5</sub> is the only halogen oxide which is stable with respect to dissociation into elements. Chlorine oxides decompose violently while the bromine oxides are the least stable among the halogen oxides. Of these only Cl<sub>2</sub>O and ClO<sub>2</sub> find some practical importance as bleaching agents in paper pulp and flour industries, I<sub>2</sub>O<sub>5</sub> is used in the estimation of CO.

Table 10.6 : Oxides of halogens

Fluorides		Oxides					
Compound	Oxidation number (O.N.)	Chlorine Compound	O.N.	Bromine Compound	O.N.	Iodine Compound	O.N.
OF <sub>2</sub>	-1	Cl <sub>2</sub> O	+1	Br <sub>2</sub> O	+1		
O <sub>2</sub> F <sub>2</sub>	-1	ClO <sub>2</sub>	+4	BrO <sub>2</sub>	+4	I <sub>2</sub> O <sub>5</sub>	+5
		Cl <sub>2</sub> O <sub>6</sub>	+6	BrO <sub>3</sub>	+6		
		Cl <sub>2</sub> O <sub>7</sub>	+7				

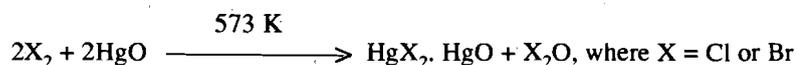
### Preparation of Halogen Oxides

Oxygen difluoride is prepared by passing fluorine into a 2% NaOH solution:

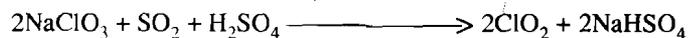


It is a stable colourless gas. It reacts vigorously with metals, sulphur, phosphorus and halogens and gives fluorides and oxides. It reacts with bases to give F<sup>-</sup> ion and free oxygen.

Cl<sub>2</sub>O and Br<sub>2</sub>O are prepared by heating freshly precipitated mercuric oxide with the halogen gas :



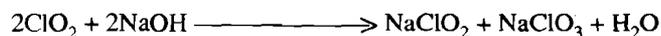
Chlorine dioxide ( $\text{ClO}_2$ ) is also prepared by the following reactions :



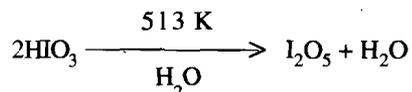
It is also obtained by treating silver chlorate with dry chlorine at 363 K :



Chlorine dioxide is a gas at normal temperature, b.p. 284 K. It is a powerful oxidising and chlorinating agent. It reacts with alkalis to form chlorites and chlorates :



Iodine pentoxide ( $\text{I}_2\text{O}_5$ ) is prepared by dehydration of iodic acid at 513 K :



It is a white solid which decomposes to iodine and oxygen above 573 K.  $\text{I}_2\text{O}_5$  is a good oxidising agent, it oxidises  $\text{H}_2\text{S}$  to sulphur and  $\text{HCl}$  to chlorine.

### Properties of Halogen Oxides

All oxides of halogens have positive free energies of formation except  $\text{F}_2\text{O}$  and are thus unstable with respect to dissociation into elements.  $\text{F}_2\text{O}$  is stable upto 475 K. A combination of kinetic and thermodynamic factors leads to the generally decreasing order of stability  $\text{I} > \text{Cl} > \text{Br}$ . The higher oxides tend to be more stable than the lower. Except for that of iodine all oxides tend to be explosive. Iodine pentoxide,  $\text{I}_2\text{O}_5$ , is white solid stable upto 575 K. Because of their oxidising properties, chlorine oxides,  $\text{Cl}_2\text{O}$  and  $\text{ClO}_2$  are used as bleaching agents and as **germicides**.  $\text{I}_2\text{O}_5$  quantitatively oxidises  $\text{CO}$  into  $\text{CO}_2$  and therefore, is used in the estimation of  $\text{CO}$ .

### Structure of Oxides of Halogens

Structures of only  $\text{OF}_2$ ,  $\text{Cl}_2\text{O}$ ,  $\text{Br}_2\text{O}$ ,  $\text{Cl}_2\text{O}_7$  and  $\text{I}_2\text{O}_5$  are definitely known. Structures of the monoxides can be explained on the basis of VSEPR theory about which you have already studied in Unit 3 of the course, **Atoms and Molecules**. These oxides have tetrahedral structure with two lone pairs on oxygen. Thus, the molecule is V shaped or angular in shape. The bond angle EOE varies in the order  $\text{FOF} < \text{ClOCl} < \text{BrOBr}$ . This is because electrons in the case of  $\text{OF}_2$  are nearer to fluorine due to high electronegativity of F compared to Cl or Br. The bonded electron pairs in  $\text{Cl}_2\text{O}$  and  $\text{Br}_2\text{O}$  are closer to oxygen making the repulsion between them more and thereby reducing the lone pair - lone pair repulsion on oxygen to some extent. Also due to the bulkiness of Cl and Br, the angles  $\text{ClOCl}$  and  $\text{BrOBr}$  increase to such an extent that they are greater than  $109^\circ 28'$ , the tetrahedral angle. Fig. 10.1 shows some of the structures of halogen oxides.

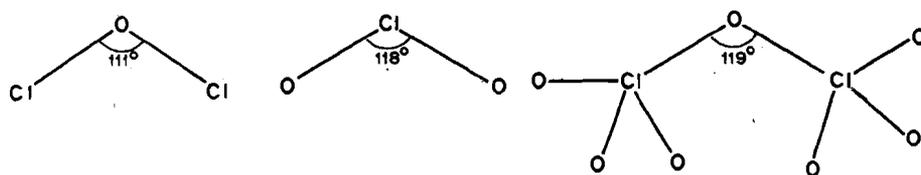


Fig. 10.1: Structures of some oxides of halogens

### 10.4.3 Oxoacids of Halogens

Oxoacids of halogens have oxygen attached to the halogen atom. They have the general formula  $\text{HOX}(\text{O})_n$  where  $n = 0, 1, 2$  or  $3$ . The oxoacids are named as hypohalous acid ( $\text{HOX}$ ), halous acid ( $\text{HOXO}$ ), halic acid ( $\text{HOXO}_2$ ) and perhalic acid ( $\text{HOXO}_3$ ), in which the oxidation state of the halogen is  $+1, +3, +5$  and  $+7$ , respectively. Most of the oxoacids are known only in solution or as salts. Fluorine being more electronegative than oxygen, does not form oxoacids except the unstable  $\text{HOF}$ . Some important oxoacids of halogens are given in Table 10.7.

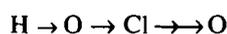
Table 10.7 : Important oxoacids of halogens

Names of the acid and their salts	Oxidation state of halogen in the acid	Oxoacids of			Structure
		Cl	Br	I	
Hypohalous, Hypohalites	+1	* HOCl Hypochlorous acid	* HOBr Hypobromous acid	* HOI Hypoiodous acid	H-O-X
Halous, Halites	+3	* HOClO Chlorous acid	* HOBrO Bromous acid		H-O-X→O
Halic, Halates	+5	* HOClO <sub>2</sub> Chloric acid	* HOBrO <sub>2</sub> Bromic acid	HOIO <sub>2</sub> Iodic acid	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{H-O-X} \rightarrow \text{O} \end{array}$
Perhalic, Perhalates	+7	HOClO <sub>3</sub> Perchloric acid	* HOBrO <sub>3</sub> Perbromic acid	HOBrO <sub>3</sub> Periodic acid	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{HO-X} \rightarrow \text{O} \\ \downarrow \\ \text{O} \end{array}$

\* Stable only in solution

The oxoacids containing higher number of oxygen atoms, i.e., having halogens in higher oxidation state are thermally more stable and are known in pure state. You may compare this with the increased stability in case of higher oxides of halogens. However, the thermal stability decreases with increase in the atomic number of the halogen. Thus, HOCl is the most stable and HOI the least stable among the hypohalous acids.

Acid strength of oxoacids increases with increase in the oxidation number of the halogen. This can be explained as follows. Because oxygen is more electronegative than halogens (consider only Cl, Br and I), the terminal oxygen atom pulls the electrons of O-X bond towards itself, leaving a slight positive charge on the halogen atom. The halogen atom then draws the electrons of X-OH bond towards itself. This oxygen atom in turn pulls the electrons of O-H bond towards itself, leaving hydrogen atom slightly positively charged and making the O-H bond more easily ionisable. This makes the compound more acidic.



It is obvious from the above that higher the oxidation number of the halogen,

- higher is the number of oxygen atoms attached to the halogen,
- more effective is the displacement of shared electrons towards the terminal oxygen atoms and
- more acidic is the oxoacid.

Acid strength of oxoacids with halogen in the same oxidation state, decreases as we go down the group. Thus HOCl is the strongest and HOI is the weakest amongst these acids. Hypoiodic acid is amphoteric and may be regarded as iodine hydroxide, IOH, in many reactions. Decrease in acid strength of corresponding oxoacids down the group may be explained on the basis of decreasing electronegativities of the halogens.

NaOCl is one of the important salts of hypochlorous acid and is used in bleaching cotton fabrics, wood pulp and also as a disinfectant.

Anhydrous perchloric acid, HClO<sub>4</sub>, is an extremely powerful oxidising agent which explodes when in contact with organic matter and sometimes on its own. Periodic acid, HIO<sub>4</sub>, is extensively used in organic chemistry for oxidation of alkenes to glycols.

#### SAQ 6

Arrange the following in the order of increasing acid strength : HOCl, HOClO<sub>2</sub>, HOClO<sub>3</sub> and HOClO.

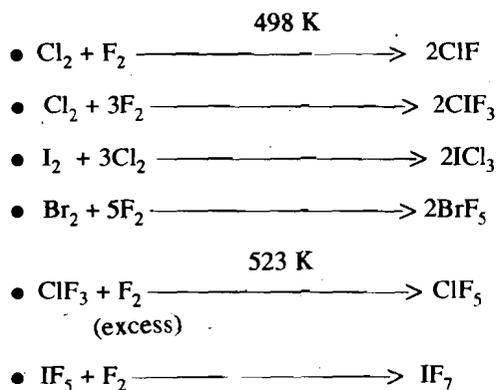
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## 10.4.4 Interhalogen Compounds

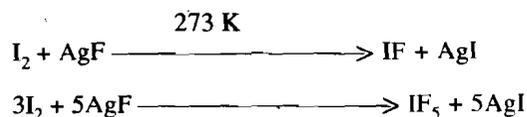
Compounds formed by the interaction of one halogen with other halogens are called **interhalogen compounds**. Such compounds are either binary, formed by a combination of two halogens or ternary, formed by a combination of three halogens. The binary compounds are of four types, viz.,  $XY$ ,  $XY_3$ ,  $XY_5$  and  $XY_7$ , where X and Y are the two halogens and Y is more electronegative than X. Interhalogen compounds are named as the halides of less electronegative halogen. Thus  $ClF$  is called chlorine monofluoride and not fluorine monochloride. Ternary interhalogen compounds were unknown until recently except as polyhalide anions or polyhalonium cations, but now some compounds, e.g.,  $IFCl_2$  and  $IF_2Cl$  have been prepared. The interhalogen compounds with fluorine are more common.

The stability of interhalogen compounds depends on the electronegativity difference of the two halogens. Greater the difference, more polar is the bond and therefore, greater is the thermal stability and higher their melting and boiling points.

The interhalogen compounds can be prepared by direct combination of the halogens or by action of the halogen on a lower interhalogen compound. A few examples are given below :



Mono- and penta-fluorides of iodine are prepared by the action of  $\text{AgF}$  on  $\text{I}_2$ :



### Properties

Some physical properties of the interhalogen compounds like colour are intermediate between those of the constituent elements but their melting and boiling points are higher than expected from interpolation of the melting and boiling points of the constituent halogens. Some properties of interhalogen compounds are given in Table 10.8.

Interhalogen compounds are generally more reactive than the halogens (except F) since  $X-Y$  bond is more polar than the  $X-X$  bond. They are hydrolysed by water or alkali to the halide ion of the lighter halogen ( $Y^-$ ) and the hypohalite ion of the heavier halogen ( $OX^-$ ). The interhalogen compounds react with alkenes and add across the double bond ( $C=C$ ). They are strong oxidising agents and are used to prepare metal halides. They convert metals into mixed halides :



Their most important use is as fluorinating agents. They are also used as non-aqueous solvents. Iodine trichloride and bromine trifluoride autoionise like water and ammonia to give polyhalide ions, e.g.,



Thus, the substances which furnish  $\text{ICl}_2^+$  and  $\text{BrF}_2^+$  behave as acids and those furnishing  $\text{ICl}_4^-$  and  $\text{BrF}_4^-$  behave as bases in  $\text{ICl}_3$  and  $\text{BrF}_3$  solvent systems, respectively.

Table 10.8 : Some interhalogen compounds

Type of interhalogen compound	Formulae and names of compounds	Physical state and colour at ordinary temperatures	Melting point (K)	Boiling point (K)
XY	ClF Chlorine fluoride	Gas, Colourless.	119	163
	BrF Bromine fluoride	Liquid below 293K, pale-brown gas above 293K	240	293
	BrCl Bromine chloride	Liquid, reddish yellow	207	283
	ICl Iodine chloride	Solid, ruby red	—	310
	IBr Iodine bromide	Solid, brown like iodine	232	—
XY <sub>3</sub>	ClF <sub>3</sub> Chlorine trifluoride	Liquid below 261K, colourless gas above 261 K	197	261
	BrF <sub>3</sub> Bromine trifluoride	Liquid, Colourless	282	400
	BrCl <sub>3</sub> Bromine trichloride	Solid, Orange	374 (decomposes)	—
XY <sub>5</sub>	ClF <sub>5</sub> Chlorine pentafluoride	Gas, Colourless	170	259
	BrF <sub>5</sub> Bromine pentafluoride	Liquid, Colourless	213	314
	IF <sub>5</sub> Iodine pentafluoride	Liquid, Colourless	283	314
XY <sub>7</sub>	IF <sub>7</sub> Iodine heptafluoride	Gas, Colourless	279.5	—

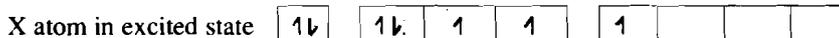
### Structure of Interhalogen Compounds

The interhalogen compounds are generally covalent in which the larger atom lies in the centre. Their shapes can be predicted by VSEPR theory about which you have already studied in Unit 3 of the "Atoms and Molecules" course. Shapes of some of the interhalogen compounds are given in Table 10.9.

Molecule	Total number of electron pairs around X	Bond pairs	Lone pairs	Shape
XY	4	1	3	Linear
XY <sub>3</sub>	5	3	2	T-shaped
XY <sub>5</sub>	6	5	1	Square pyramidal
XY <sub>7</sub>	7	7	0	Pentagonal bipyramidal

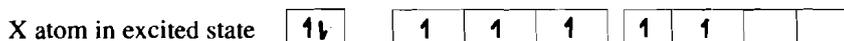
Structures of interhalogens can be explained with the help of Valence Bond Theory also in the following manner :

- Type XY : As expected, the compounds of the type XY are linear (Fig.10.2). Thus ClF, BrF, BrCl, IBr and ICl all have a linear structure. In these compounds both the halogen atoms have an unpaired electron in the  $p_z$  orbital. Axial overlap of the  $p_z$  orbitals of the two halogen atoms results in a linear interhalogen molecule.
- Type XY<sub>3</sub> : Structure of the interhalogens of this type can be explained on the basis of  $sp^3d$  hybridisation of the central halogen atom X. Three of the hybrid orbitals having an electron each are used in making three covalent bonds with three atoms of the other halogen atom. The remaining two orbitals accommodate the two lone pairs of the central atom. In order to minimise lone pair-lone pair and lone pair-bond pair repulsions, the lone pairs occupy the two equatorial sites around the central halogen atom, thereby giving a T-shape to the molecule (Fig. 10.3). Thus ClF<sub>3</sub>, BrF<sub>3</sub> and ICl<sub>3</sub> have a T-shaped structure.



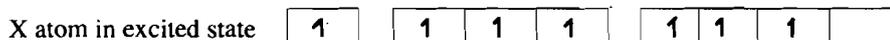
$sp^3d$  hybridisation – trigonal bipyramidal structure with two equatorial sites occupied by lone pairs.

- Type XY<sub>5</sub> : This type of compounds have a square pyramidal structure (Fig.10.4). The central atom X uses five of its seven valence electrons in forming five bonds with Y and two electrons remain as a lone pair. Thus X-atom in XY<sub>5</sub> molecule is  $sp^3d^2$  hybridised. The lone pair occupies the axial hybrid orbital.



$sp^3d^2$  hybridisation – octahedral structure with one of the axial sites occupied by lone pair.

- Type XY<sub>7</sub> : In these molecules, the central X atom uses all its seven valence electrons in forming seven X–Y bonds. Formation of this type of compounds can be explained on the basis of  $sp^3d^3$  hybridisation of the X atom. These compounds have a pentagonal bipyramidal structure with two axial X–Y bonds and five equatorial X–Y bonds (Fig. 10.5).



$sp^3d^3$  hybridisation – pentagonal bipyramidal structure.

### 10.4.5 Polyhalides and Polyhalonium Ions

Halide ions often associate with molecules of halogens or with interhalogen compounds to form polyhalide ions. For example, on addition of potassium iodide, the solubility of iodine in water is greatly enhanced due to the formation of the triiodide ion, I<sub>3</sub><sup>-</sup>:



Fig. 10.2: Linear structure of interhalogen molecule of the type XY.

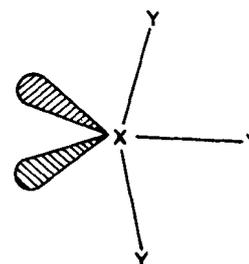


Fig. 10.3: T-shaped structure of interhalogen molecules of the type XY<sub>3</sub>.

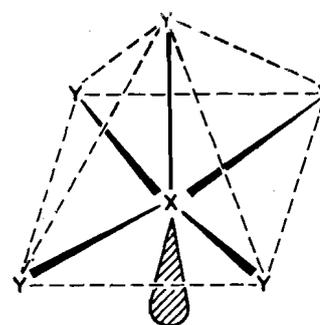


Fig 10.4: Square pyramidal structure of interhalogen molecules of the type XY<sub>5</sub>.

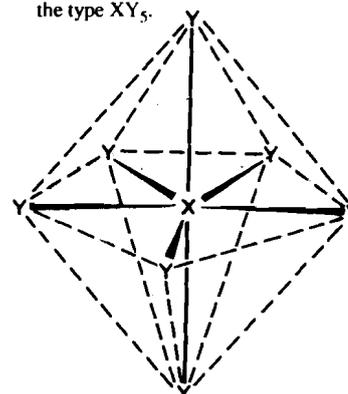


Fig. 10.5 : Pentagonal bipyramidal structure of interhalogen molecules of the type XY<sub>7</sub>.

More complex ions of iodine, such as penta-iodide,  $I_5^-$ , hepta-iodide,  $I_7^-$  and nona-iodide,  $I_9^-$  are also known.

These are generally found in the form of salts of large metal ions, e.g.,  $Rb^+ I_9 \cdot 2C_6H_6$  or large complex cations, e.g.,  $NH_4^+ I_5^-$ ,  $(C_2H_5)_4 N^+ I_7^-$ . A number of mixed polyhalide ions containing two or three different halogens are also known, e.g.,  $ICl_2^-$ ,  $ICl_4^-$  and  $I\text{BrF}^-$  and  $I\text{BrCl}^-$ .

All the polyhalides are hydrolysed to some extent in aqueous solution. The ease of hydrolysis increases with the introduction of the more electronegative halogen, into the ion. Thus, the triiodide being the most stable and  $ClI^-$  the least. In non-aqueous solutions, polyhalides behave as mild halogenating agents.<sup>3</sup>

You have learnt in Section 10.4.4 that polyhalonium cations, e.g.,  $ICl_2^+$  and  $BrF_2^+$  are formed as a result of autoionisation of  $ICl_3$  and  $BrF_3$ . Other cations like  $Br_2^+$ ,  $I_2^+$ ,  $I_3^+$ ,  $ClF_2^+$ ,  $IF_2^+$ ,  $I\text{Br}_2^+$ ,  $I\text{BrCl}^+$ ,  $ClF_4^+$ ,  $BrF_4^+$ ,  $IF_4^+$ ,  $ClF_6^+$ ,  $BrF_6^+$ ,  $IF_6^+$ , etc. are also known. These are established by large anions like  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $AlCl_4^-$ ,  $SbCl_6^-$ , etc.

### SAQ 7

Write 'T' for true and 'F' for false in the given boxes for the following statements about the interhalogen compounds.

- |   |                          |
|---|--------------------------|
| i) Interhalogen compounds are strong oxidising agents       | <input type="checkbox"/> |
| ii) Interhalogen compounds are strong reducing agents       | <input type="checkbox"/> |
| iii) X–Y bond is more polar than X–X and Y–Y bonds          | <input type="checkbox"/> |
| iv) Interhalogen compounds are ionic                        | <input type="checkbox"/> |
| v) $XY_3$ type of molecules have square pyramidal structure | <input type="checkbox"/> |

## 10.5 PSEUDOHALOGENS AND PSEUDOHALIDES

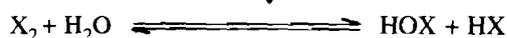
Some molecules like cyanogen,  $(CN)_2$ , thiocyanogen,  $(SCN)_2$  and selenocyanogen,  $(SeCN)_2$ , have properties similar to those of the halogens. Therefore, these are called pseudohalogens. Pseudohalogens form hydro acids similar to the hydrohalic acids, e.g.,  $H-CN$ . They also form anions such as cyanide,  $CN^-$ , cyanate,  $OCN^-$ , thiocyanate,  $SCN^-$ , selenocyanate,  $SeCN^-$ , tellurocyanate,  $TeCN^-$  and azide,  $N_3^-$ , which resemble the halide ions to some extent.

The best known pseudohalide is the cyanide,  $CN^-$ , which resembles  $Cl^-$ ,  $Br^-$  and  $I^-$  in the following respects :

- It can be oxidised to form a molecule,  $(CN)_2$ .
- It forms an acid  $HCN$  similar to  $HCl$ ,  $HBr$ , etc.
- It forms insoluble salts with  $Ag^+$ ,  $Pb^{2+}$  and  $Hg^+$ .
- Interpseudohalogen compounds  $ClCN$ ,  $BrCN$  and  $ICN$  can also be formed.
- Like  $AgCl$ ,  $AgCN$  is insoluble in water but soluble in liquor ammonia.
- It forms a large number of complexes similar to the halide complexes, e.g.,  $[Cu(CN)_4]^{2-}$  is similar to  $[CuCl_4]^{2-}$  and  $[Co(CN)_6]^{3-}$  is similar to  $[CoCl_6]^{3-}$ .

Fluorine differs from other elements of the group because of its exceptionally small atomic and ionic size and low fluorine—fluorine bond dissociation energy. The result of these differences is that fluorine is the most electronegative element in the periodic table and is a powerful oxidant. Some differences between fluorine and other halogens are :

- It is more reactive than other halogens because of low F-F bond energy, also due to its high electronegativity the bond between fluorine and other elements is very strong so its compounds are more stable. Some of them are inert, e.g., SF<sub>6</sub>.
- Fluorine is almost invariably monocoordinate (coordination number = 1) and is never more than mono covalent.
- Fluorides are more ionic.
- Fluorine forms strong hydrogen bonds resulting in the properties of hydrogen fluoride being anomalous.
- Fluorine is the strongest oxidising agent and oxidises the elements to their highest oxidation state, for example in IF<sub>7</sub>, iodine has oxidation number seven.
- The reactions of fluorine are also different from other halogens. Fluorine fumes in moist air and decomposes water to give oxygen, whereas other halogens are sparingly soluble in water and react partly to give hydrohalic and hypohalous acids.



- Fluorine reacts with alkalis to yield the oxide, F<sub>2</sub>O :



The other halogens react with alkalis to yield a solution of hypohalite ions, which may disproportionate. The oxoacid of fluorine, HOF, prepared recently is very unstable. The oxides of fluorine are not acidic.

## 10.7 SUMMARY

Let us now summarise what we have learnt in this unit.

- The halogens are only one electron short of the noble gas configuration.
- The elements form the anion X<sup>-</sup> or a single covalent bond. Their chemistry is completely non-metallic though there is some evidence of their forming cations.
- Their chemical and the physical properties show variations according to the expected group trends.
- Because of the extremely small size of fluorine, it exhibits anomalous behaviour in the F-F bond energy and electron affinity.
- Fluorine is the strongest oxidising agent in the whole group. This is mainly because of very low F-F bond energy, very high F-element bond energy and the high hydration energy of the fluoride ion.
- Fluorine can oxidise all the other halide ions like Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> to their respective elements. Because of its high oxidising power, fluorine forms compounds in which the other elements are in high oxidation states.
- The oxidation state of fluorine is -1 while the other halogens exhibit variable oxidation states due to the availability of vacant *d* orbitals.
- Halogens form a variety of compounds like, hydrohalic acids of the type HX, halogen oxides (OX<sub>2</sub> etc.), oxoacids like HOX, HC XO, HOXO<sub>2</sub> and HOXO<sub>3</sub> and interhalogen compounds of the type XY<sub>n</sub> where X and Y are two different halogens. The bond in interhalogen compounds is polar with a positive charge on the heavier halogen. You have also learnt about the polyhalide ions, X<sub>n</sub><sup>-</sup> and XY<sub>n</sub><sup>-</sup>.

## 10.8 TERMINAL QUESTIONS

- Fill the appropriate halogen in the following blanks :
  - \_\_\_\_\_ displaces three halogens from their compounds.
  - $\text{Cl}^-$  can be oxidised by \_\_\_\_\_
  - $\text{Br}_2$  can be reduced by \_\_\_\_\_
  - Fluorine and \_\_\_\_\_ can oxidise water to oxygen .
  - Oxidation of \_\_\_\_\_ and \_\_\_\_\_ by  $\text{Cl}_2$  will give  $\text{Br}_2$  and  $\text{I}_2$ , respectively.
- We have listed the physical properties of all the halogens except astatine in Table 10.1. From your study of the periodicity in the properties of elements, predict the following for the astatine :
  - Atomic number
  - Molecular formula
  - M.P., B.P:
  - Physical state
  - At-At bond energy
  - Strength of aqueous hydroastatic acid.
- Why does fluorine combine with other elements in their higher oxidation states.
- Write the name of the following oxoacids and deduce the oxidation number of halogen atom in each.
 

(i) $\text{HOCl}$	(ii) $\text{HOClO}$	(iii) $\text{HOBr}$
(iv) $\text{HOBrO}_2$	(v) $\text{HOIO}_3$	(vi) $\text{HOClO}_3$
- The bond dissociation energy increases from  $\text{I}_2$  to  $\text{Cl}_2$ . Thus, bond dissociation energy of  $\text{F}_2$  should be higher than that of  $\text{Cl}_2$ . But it is not so, why?
- The solutions of the salts of hypohalous acids are alkaline, explain why?

## 10.9 ANSWERS

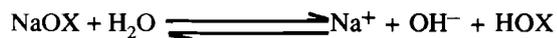
### Self-Assessment Questions

- Fluorine formed by the electrolysis of aqueous solution of  $\text{NaF}$  will react immediately with water so it cannot be obtained by this method.
- Chlorine
  - Iodine
  - Fluorine
  - Iodine
- The standard reduction potentials of bromine and iodine are 1.07 and 0.54, respectively, which are less than that for reduction of oxygen to water. These elements, therefore, can not oxidise water to oxygen.
- |  |        |   |
|--|--------|---|
| i) $\text{I}_2 + \text{IF}_3$          | —————→ | 3IF   |
| ii) $\text{Cl}_2 + \text{H}_2\text{O}$ | —————→ | $\text{HCl} + \text{HOCl}$                        |
| iii) $\text{Cl}_2 + 2\text{NaOH}$      | —————→ | $\text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}$ |
| iv) $\text{Cl}_2 + \text{H}_2\text{S}$ | —————→ | $2\text{HCl} + \text{S}$                          |
| v) $\text{CH}_4 + 4 \text{Br}_2$       | —————→ | $\text{CBr}_4 + 4\text{HBr}$                      |

- 5 HF has the highest bond dissociation enthalpy amongst all the halogen acids. The hydration enthalpy of the fluoride ion is also highest. However, the former outweighs making HF the weakest of the halogen acids.
- 6  $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$
- 7 (i) T (ii) F (iii) T  
(iv) F (v) F

### Terminal Questions

- 1 i) Fluorine ii) Fluorine iii)  $\text{F}^-$   
iv) Chlorine v)  $\text{Br}^-$  and  $\text{I}^-$
- 2 i) Atomic number should be 85.  
ii)  $\text{At}_2$ .  
iii) Melting and boiling point should be higher than those of iodine.  
iv) Solid.  
v) At-At bond energy should be less than that of I-I bond.  
vi) Strength of aqueous hydroastatic acid should be highest according to known trend  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ .
- 3 The highest oxidising power, high lattice energy of fluorides and high enthalpy of hydration of fluoride ion, lower F-F bond dissociation energy and a high fluorine element covalent bond energy are the factors contributing to this unique ability of fluorine to combine with other elements in their higher oxidation states. Chlorine, however, is a close second in this respect.
- 4 i) Hypochlorous acid : +1  
ii) Chlorous acid : +3  
iii) Hypobromous acid : +1  
iv) Bromic acid : +5  
v) Periodic acid : +7  
vi) Perchloric acid : +7
- 5 Fluorine has the smallest size of all the halogens. In the F-F bond, there is considerable repulsion in the nonbonding electrons which weakens the F-F bond. Therefore, the bond dissociation energy of  $\text{F}_2$  is less than that of the  $\text{Cl}_2$ .
- 6 The salts of hypohalous acids undergo hydrolysis in water as shown below :



The hypohalous acids are fairly weak acids and remain largely undissociated in solution. As the solution contains  $\text{OH}^-$ , it becomes alkaline in nature.

# UNIT 11 ELEMENTS OF GROUP 18

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## Structure

- 11.1 Introduction
    - Objectives
  - 11.2 Discovery of Noble Gases
    - Position of Noble Gases in the Periodic Table
  - 11.3 Occurrence, Isolation and Uses of Noble Gases
  - 11.4 General Characteristics
  - 11.5 Compounds of Noble Gases
    - Compounds of Xenon
    - Clathrates of Noble Gases
    - Structure and Bonding in Xenon Compounds
    - Structure of Noble Gas Compounds and VSEPR Theory
  - 11.6 Summary
  - 11.7 Terminal Questions
  - 11.8 Answers
- 

## 11.1 INTRODUCTION

---

In the preceding unit, you have learnt about the chemistry of a group of highly reactive elements, viz., the halogens. This unit deals with the chemistry of a group of elements which were considered to be rather inert till recently. These elements are helium, neon, argon, krypton, xenon and radon. These elements constitute Group 18 of the modern periodic table. If you compare Mendeleev's periodic table of 1871 with the modern periodic table, you will see that it is remarkably similar in its coverage to the modern periodic table, with the exception that the Group 18 is missing. Elements of Group 18 were not known at that time and have been discovered only about a hundred years back. Since these elements have very low reactivity, they were called inert. However, the term inert is no longer applicable to the group as a whole, as the heavier elements of this group form compounds and, thus, are not inert. These elements have also been called the rare gases, but as argon forms nearly 1% of the atmosphere, and the gases can be readily isolated by the fractional distillation of liquid air at low temperatures, this name is also not very appropriate. They are now called the noble gases by analogy with the noble metals, like gold and platinum which are not very reactive. The unique chemical inertness of the noble gases is well reflected in the history of their discovery which was followed by a long gap of a few decades before xenon could be made to combine with only the most electronegative elements, fluorine and oxygen. In this unit you will study the discovery, isolation, uses, general characteristics and the compounds of noble gases.

### Objectives

After studying this unit, you should be able to :

- describe the discovery of noble gases,
  - discuss their electronic configuration and position in the periodic table,
  - enumerate the properties of the noble gases and their uses, and
  - describe the important compounds of the noble gases, particularly xenon, especially the bonding in these compounds.
- 

## 11.2 DISCOVERY OF NOBLE GASES

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The story of the discovery and investigation of the noble gases is one of the most brilliant and interesting chapters in the history of science. Their discovery can be traced back to 1785, when Henry Cavendish investigated the composition of air. He mixed excess oxygen with air and then passed electric sparks through the mixture. The oxides of nitrogen, thus formed, were removed by dissolving in alkali solution and the excess of oxygen was removed with potassium sulphite. The residual gas, which was always left behind, was neither nitrogen nor oxygen. It did not form more than 1/120th part of the original volume of air. Time was not