

Unit 4.4 Chemistry of Non-transition Elements

Few facts of halogens:

- Ionisation energy of halogens is very high. This indicates that it has very little tendency to lose electrons. Due to gradual increase in size, it decreases down the group.
- The halogen molecules are held by weak Vander Waals forces, which increase down the group. This is responsible for the solid state of iodine.
- Chlorine has highest electron affinity in the group. Due to small size, fluorine has lower electron affinity than chlorine.
- All halogens are coloured as shown below:

Halogens	Fluorine	Chlorine	Bromine	Iodine
Colour	Light Yellow	Greenish Yellow	Reddish Yellow	Dark Violet

The origin of colours of halogens is due to the absorption of visible light which excite the outermost electron to a higher energy level. Fluorine, being very small in size require very large excitation energy (obtained from the blue or violet part) of light, hence light yellow. Iodine being very large in size, the required lower excitation energy is obtained by absorption of yellow part of light.

Interhalogen compounds:

Halogen elements have different electro-negativity. Due to this they combine with each other to form covalent compounds (binary).

“The binary compounds formed by halogens amongst themselves are known as Inter-halogen compounds”. These compounds have general formula; XY_n , where $n = 1, 3, 5 \text{ \& } 7$.

Ternary compounds of halogens are not known; as such a complex molecule might be unstable.

Classification: Various types of inter-halogen compounds are tabulated below:

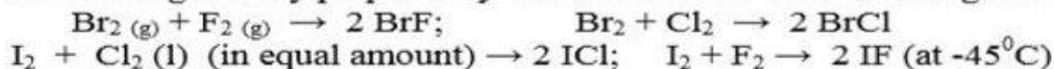
Element	Fluorine	Chlorine	Bromine	Iodine
Fluorine	-----	-----	-----	-----
Chlorine	ClF, ClF_3, ClF_5	---	---	---
Bromine	BrF, BrF_3, BrF_5	$BrCl$	---	---
Iodine	IF, IF_3, IF_5, IF_7	ICl, ICl_3	IBr	---

From the above table, the following points may be noted:

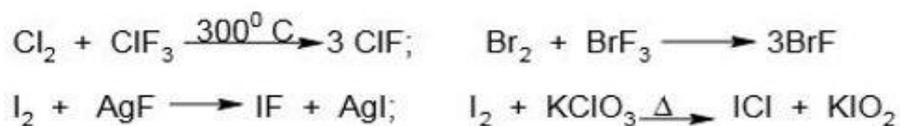
- The inter-halogen compounds may be regarded as the halide of the more electronegative halogen. Thus, since the electro positive character of halogens is in the order $F < Cl < Br < I$, fluorine cannot form any inter-halogen compounds, while iodine has the maximum tendency to form inter-halogen compounds.
- Since F has the least electropositive character, amongst inter-halogen compounds, the fluorides are maximum in number.
- Inter-halogens can be grouped into four categories: XY, XY_3, XY_5 , and XY_7 . Here X halogen atom is more electropositive and larger in size than Y halogen atom.
- The oxidation state of atom X in XY, XY_3, XY_5 , and XY_7 molecules is equal to +1, +3, +5 and +7 respectively.
- As the ratio between the radii of X and Y atoms increases, the number of halogen atoms per molecule increases.

I. Inter-halogen compounds of XY type (Diatomic inter-halogens): Preparation:

➤ These are generally prepared by the direct combination of halogens e.g.,



➤ Some of them can be prepared by other methods,

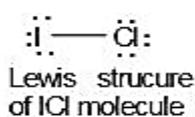


Properties:

- i. These are covalent gases because of small difference in electro-negativities between the two halogen atoms.
- ii. *Stability:* They differ in thermal stability. For example, ClF is extremely stable and dissociate when heated strongly:
 $2 \text{ClF} \rightarrow \text{Cl}_2 + \text{F}_2$, while IBr dissociate to a small extent into I_2 and Br_2 when heated.
BrF and IF are unstable and undergo disproportionation rapidly.
 $3 \text{BrF} \rightarrow \text{Br}_2 + \text{BrF}_3$; $5 \text{IF} \rightarrow 2 \text{I}_2 + \text{IF}_5$
The stability of XY type inter-halogen compounds with respect to disproportionation is in the order:
 $\text{ClF} > \text{ICl} > \text{IBr} > \text{BrCl} > \text{BrF}$
- iii. *Hydrolysis:* Generally hydrolysis of these compounds give oxy acids and hydrohalic acid. For example:
 $\text{BrCl} + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HCl}$
 $5\text{ICl} + 3\text{H}_2\text{O} \rightarrow \text{HIO} + 5\text{HCl} + 2\text{I}_2$; $\text{ICl} + \text{H}_2\text{O} \rightarrow \text{HOI} + \text{HCl}$
- iv. *Action of metals and non-metals:*
 $\text{Se} + 4 \text{ClF} \rightarrow \text{SeF}_4 + 2 \text{Cl}_2$; $\text{ICl} + 2\text{Na} \rightarrow \text{NaI} + \text{NaCl}$
 $\text{W} + 6 \text{ClF} \rightarrow \text{WF}_6 + 3 \text{Cl}_2$
- v. *Action of alkali metal halides and olefins:* With alkali metal halides, polyhalides are formed while inter-halogens add to olefins at double bond sites.
 $\text{KCl} + \text{ICl} \rightarrow \text{K}[\text{ICl}_2]$; $\text{NaBr} + \text{IBr} \rightarrow \text{Na}[\text{IBr}_2]$
$$\text{—CH=CH—} + \text{ICl} \longrightarrow \begin{array}{c} \text{—CH—CH—} \\ | \quad | \\ \text{I} \quad \text{Cl} \end{array}$$
- vi. *Lewis acid strength:* The Lewis acid strength of these compounds decreases in the order: $\text{ICl} \gg \text{BrCl} > \text{IBr} > \text{I}_2$ *Reactivity:* These compounds are more reactive than each of the halogen molecules because X-Y bond dissociation energy is less than that of X-X bond.

Structure and geometry of XY type Inter-halogen compounds:

Examples of such compounds are ClF, BrF, IF, BrCl, ICl and IBr. Let us consider example of ICl molecule in which I-atom is the central atom. All these molecules have *linear geometry* which arises because of sp^3 hybridisation of the central halogen atom, iodine.



Lewis structure of this molecule shows that the central I-atom is surrounded by three lone pairs of electrons and one σ -bonding electron pair. Thus I-atom is sp^3 hybridised in ICl molecule.

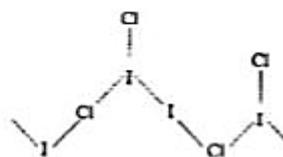
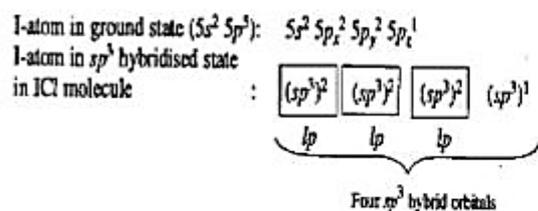


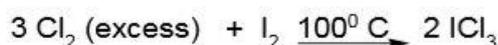
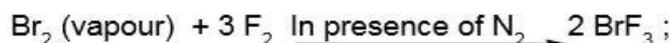
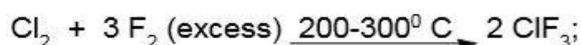
Fig. 3.1 Zig-zag chain of ICl molecule in its α and β -form

I-Cl σ -bond results by the head-to-head overlap between the singly-filled $3p_z$ orbital of Cl-atom and singly filled sp^3 hybrid orbital on I-atom. Although the spatial arrangement of 4-electron pairs round I-atom is tetrahedral, due to the presence of three lone pairs of electrons, the shape of ICl molecule gets distorted and becomes linear. ICl molecule form zig-zag chains in both α and β -form. Both forms differ only whether Cl-branches are cis (α) or trans (β).

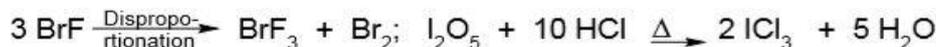
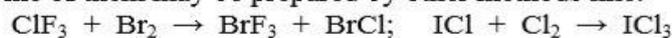
II-Inter-halogen compounds of XY₃ type (Tetra-atomic inter-halogens):

Preparation:

- These are generally prepared by direct combination of elements under suitable conditions.

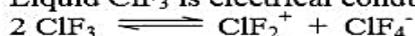


- Some of them may be prepared by other methods like:

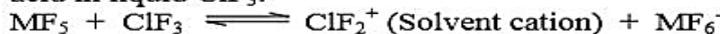


Properties: Among these XY₃ type compounds, ClF₃ is the most reactive.

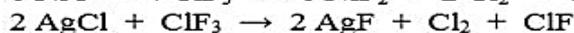
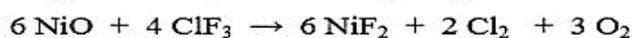
- It is colourless gas which condenses to give a pale green liquid of b. p. -12^o C.
- It is the most reactive of all XY₃ type compounds and reacts with inert substance also. It ignites material like wood, asbestos etc.
- Liquid ClF₃ is electrical conductor which suggest its auto-ionisation.



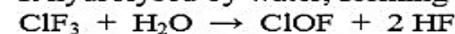
It is obvious from the following reaction that MF₅ (M=As, Sb, V) acts as an acid in liquid ClF₃.



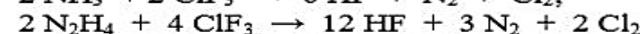
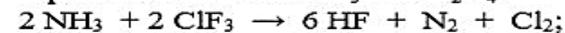
It acts as fluorinating agent as follow.



- It hydrolysed by water, forming ClOF.



- It produced HF with NH₃ and N₂H₄.



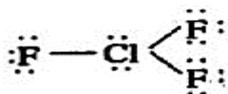
- With F₂ gives higher inter-halogens.



Uses: ClF₃ is used as fluorinating agent for preparation of number of metal fluoride, for preparation of metallic polyhalides and in cutting oil well tubes.

Structure and geometry of XY₃ type Inter-halogen compounds:

Examples of such compounds are ClF₃, BrF₃ and IF₃. All these molecules have bent T-shaped structure which is due to sp³d hybridization of the central bigger atom. Let us discuss the geometry of ClF₃ molecule in which Cl-atom is the central atom. Lewis structure of ClF₃ molecule shows that the central Cl-atom is surrounded by three σ-bps and two lone pairs of electrons and hence Cl-atom is sp³d hybridized in ClF₃ molecule. Each of the three Cl-F σ-bonds results by the overlap of singly-filled sp³d hybrid orbital on Cl-atom and singly-filled 2pz orbital of F-atom.



Lewis structure of ClF₃ molecule

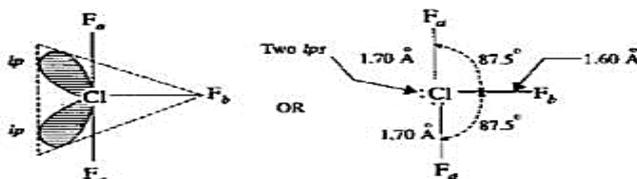
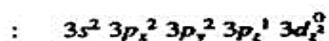
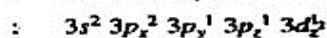


Fig. 3.2 Bent T-shaped structure of ClF₃ molecule

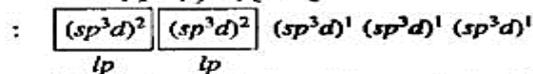
Cl-atom in ground state (3s² 3p⁵ 3d⁰)



Cl-atom in excited state (3s² 3p⁴ 3d¹)



Cl-atom in sp³d hybridised state in ClF₃ molecule



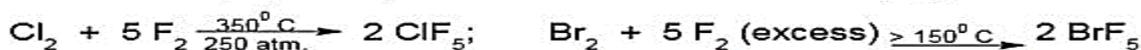
Five sp³d hybrid orbitals

Although the spatial arrangement of five electron pairs round the central Cl atom in space is trigonal bipyramidal, due to presence of two lone-pairs of electrons, the shape of ClF₃ molecule gets distorted and becomes slightly bent T-shaped. The repulsion between two lps of electrons reduces F(a)-Cl-F(b) bond angle from 90° to 87.5°. The basal Cl-F(b) bond length is equal to 1.60 Å while each of two axial Cl-F(a) bond length is equal to 1.70 Å.

Inter-halogen compounds of XY₅ type (Hexa-atomic inter-halogen):

Preparation:

➤ These are prepared by direct combination of elements, e.g.,



➤ These can also be prepared by other methods, e.g.,



Structure and geometry of XY₅ type Inter-halogen compounds:

Examples of such compounds are ClF₅, BrF₅ and IF₅. All these molecules have distorted octahedral (square pyramidal) structure which arises from sp³d² hybridization of the central atom.

Although the spatial arrangement of six electron pairs round I-atom in space is octahedral, due to the presence of one lone pair of electrons the shape of molecule gets distorted and hence IF₅ assumes square pyramidal shape.

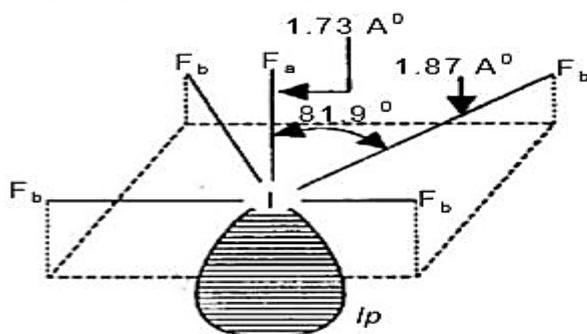


Fig. 3.6 Square pyramid structure of IF₅ molecule

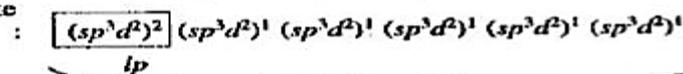
I-atom in ground state



I-atom in the excited state



I-atom in sp³d² hybridised state in IF₅ molecule



Six sp³d² hybrid orbitals

IV. Inter-halogen compounds of XY₇ type (Octa-atomic inter-halogen):

Only one compound, IF₇ of this type has been found and characterized. The reason is that an iodine atom has largest size among halogens, while F-atom has the smallest size.

It is prepared by the action of F₂ on IF₅, KI or PbI₂.



Properties:

- i. It is gas at room temperature and highly reactive.
- ii. At 250° C, with SiO₂ and Pyrex glass it gives SiF₄.

$$\text{IF}_7 + \text{SiO}_2 \rightarrow 2 \text{IOF}_3 + \text{SiF}_4$$
- iii. Vapour of IF₇ hydrolyzed by water, giving HF and H₅IO₆

$$\text{IF}_7 + 6 \text{H}_2\text{O} \rightarrow \text{H}_5\text{IO}_6 + 7 \text{HF}$$
- i. It form adducts with SbF₅ and AsF₅. These adducts are ionic compounds having the structure [IF₆]⁺[SbF₆]⁻ and [IF₆]⁺[AsF₆]⁻ respectively.

Structure and geometry of XY_7 type Inter-halogen compounds:

IF_7 is the only inter-halogen compound of this type. The Lewis structure of this molecule shows that the central I-atom is surrounded by seven σ -bps and hence I-atom in its excited state is sp^3d^2 hybridized in IF_7 molecule.

Each of the seven I-F σ -bonds is formed by the overlap between the singly-filled sp^3d^2 hybrid orbital on I-atom and singly-filled $2p_z$ orbital in F-atom. Since there is no lone pair of electrons in any of the hybrid orbital, IF_7 molecule has expected pentagonal bipyramidal shape. IF_7 molecule has two equal axial, I-F_a bonds and

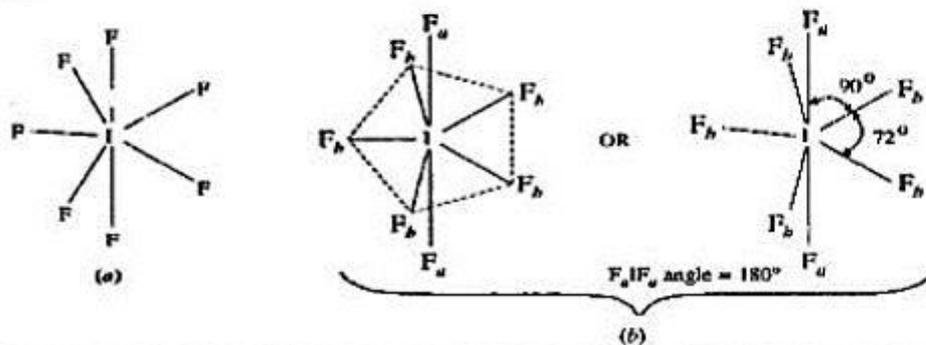


Fig. 3.8 (a) Lewis structure of IF_7 , (b) Pentagonal bipyramidal geometry of IF_7 molecule.