B.Sc. Part-I (Hons.), Paper-IB (Inorganic Chemistry)

Group-B, Unit-3 Chemistry of Halogens [By Dr. Birendra Kumar, Maharaja College]

⇒ Interhalogen Compounds

The binary compounds of halogens with one another are called interhalogen or interhalogen compounds. They are of four types: AB, AB_3, AB_5 and AB_7 (where A & B are different halogens).

1. AB type: Two halogens are in 1:1 (mole) ratio. e.g., ClF, BrF, BrCl, ICl, IBr. (maybe FrCl)
2. AB_3 type: Two halogens are in 1:3 (mole) ratio, higher En halogen (B). e.g. ClF_3, BrF_3, IF_3, ICl_3
3. AB_5 type: Two halogens are in 1:5 (mole) ratio, higher En halogen (B) is F. e.g., IF_5, BrF_5 etc.
4. AB_7 type: Two halogens (I & F) are in 1:7 (mole) ratio, higher En halogen (B) is F. Only example of this type is IF_7.

Methods of Preparation: 1. All the interhalogens (except IF_7) can be prepared by the direct combination of halogens (different) under appropriate conditions.

e.g. $Cl_2 + F_2 \xrightarrow{200^\circ C} 2ClF$; $Cl_2 + 3F_2 \xrightarrow{300^\circ C} 2ClF_3$ (excess)

(Chlorine fluoride) (Chlorine trifluoride)

$I_2 + Cl_2(l) \xrightarrow{\Delta} 2ICl$; $Br_2 + 5F_2 \xrightarrow{\Delta} 2BrF_5$ (excess)

(Iodine Chloride) (Bromine pentafluoride)

2. Higher interhalogens can be prepared from reaction of the lower interhalogens with halogen. e.g. $ClF_3 + F_2 \xrightarrow{>200^\circ C} ClF_5$; $IF_5 + F_2 \xrightarrow{260^\circ C} IF_7$

(Chlorine trifluoride) (Chlorine pentafluoride) (Iodine heptafluoride)

$BrF_3 + F_2 \xrightarrow{200^\circ C} BrF_5$

(Bromine trifluoride) (Bromine pentafluoride)

Properties: 1. ClF, BrF, BrCl, ClF_3, IF_7 etc. are covalent gases; BrF_3, BrF_5, IF_5 etc. are liquids and ICl, IBr, IF_3, ICl_3 etc. are solids.

2. All interhalogens are diamagnetic and have very low heat of formations.

3. The interhalogens (AX_n) are generally more reactive than the halogens (X_2) (except F) because A-X bond is weaker than X-X bond in the halogens.

4. Interhalogens under hydrolysis to give halide (X^-) and oxyhalide (OX^- or XO_n^-) ions. Oxyhalide ion being formed from the larger/less En halogen present.

e.g. $BrF_5 + H_2O \longrightarrow 5F^- + BrO_3^-$; $ICl + H_2O \longrightarrow Cl^- + \bar{O}I$ / IO_3^- (Iodate)

(Fluoride) (Bromate) (Chloride) (Hypoiodide)

5. Interhalogens fluorinate many metals, metal oxides & metal halides.

e.g. $MO + BrF_3 \longrightarrow MF_2 + Br_2 + O_2$; $KCl + ICl \longrightarrow KICl_2$

6. The diatomic interhalogens (ICl) add to olefines to give addition compounds.

e.g. $H_2C=CH_2 + ICl \longrightarrow H-\underset{I}{\underset{|}{C}}H-\underset{Cl}{\underset{|}{C}}H-H$

(Ethene) (1-Chloro-2-iodoethane)

(ICl/IF_5) Complex salts

It also forms addition compounds, e.g. polyhalides with alkali halides.

e.g. $ICl + NaBr \longrightarrow NaBrICl$; $IF_5 + KI \longrightarrow K[IF_6]$.

7. Liquid BrF_3, IF_5 self ionize and conduct electricity.

$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$; $IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

Uses: ICl → It is used as Wij's reagent in the estimation of the iodine number as the measure of unsaturation (C=C) of oils & fats, to iodinate organic compounds and as a catalyst.

Liq. BrF_3 → It is used as solvent in various reactions.

BrF_3 & ClF_3 → They are used as fluorinating agents for preparation of metal fluorides.

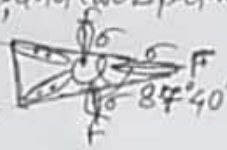
BrF_3, ClF_3, ICl_3 & ICl → They are used for preparation of polyhalides.

Stereochemistry: AB_3 type (e.g., ClF_3): In ClF_3, Cl is the central atom (outer ele. conf. $3s^2 3p^5$)

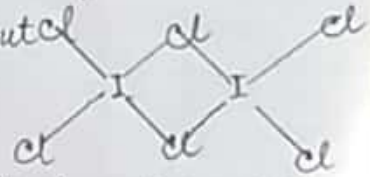
Ele. Conf. of Cl_{17} in excited state: [↑↓][↑↓][↑][↑][ ][ ][ ] ; F_9: [↑↓][↑↓][↑↓][↑]
3s 3p 3d 2s 2p

sp^3d hybridisation (5 sp^3d hybrid orbitals)

Out of five sp^3d hybrid orbitals of Cl, three sp^3d (two equitorial & one planer) hybrid orbitals of Cl overlap with $2p_z$ orbital of F-atoms forming Cl–F bonds, and two sp^3d hybrid orbitals (planar) remain unbonded as lone pair. Geometry: Trigonal bipyramid, shape: T-shaped, Bond angle = 87°40' (≈ 90). Distortion of geometry is due to the lone pairs.



ICl_3 disproportionates quite readily in the gaseous state, but in solid state two T-shaped ICl_3 molecules join together forming dimer $(ICl_3)_2$, which is flat.



AB_5 type (e.g., IF_5): In IF_5 vapours, I is the central atom (outer ele. conf. $5s^2 5p^5$)

Ele. Conf. of I_{53} in excited state (presence of 5 F-atoms): [↑↓][↑][↑][↑][↑][ ][ ] ; F_9: [↑↓][↑↓][↑↓][↑]
5s 5p 5d 2s 2p

sp^3d^2 hybridisation (6 sp^3d^2 hybrid orbitals)

Out of 6 sp^3d^2 hybrid orbitals of I, five sp^3d^2 hybrid orbitals overlap with $2p_z$ orbital of F-atoms forming I–F bonds and one sp^3d^2 hybrid orbital remains unbonded as lone pair. Geometry: Octahedral, Shape: Square pyramid. Bond angle = 90°.

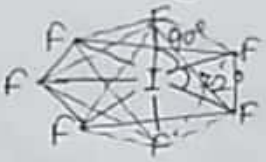
AB_7 type (e.g., IF_7): IF_7 has I as central element (outer ele. conf. $5s^2 5p^5$)

Ele. Conf. of I_{53} in excited state (in presence of 7 F-atoms): [↑↓][↑][↑][↑][↑][↑][↑][ ]
5s 5p 5d

sp^3d^3 hybridisation

F_9: [↑↓][↑↓][↑↓][↑]
2s 2p

All the 7 sp^3d^3 hybrid orbitals of I-atom overlap with $2p_z$ orbital of F-atoms forming I–F bonds. The geometry and shape of the IF_7 molecule is pentagonal bipyramid. Bond angles: 72° (plane), 90° (vertical)



—— o ——