B Sc. PART I

INORGANIC CHEMISTRY

HALOGEN GROUP

PSEUDOHALOGENS

When two or more P-block elements combine together with a unit negative charge, they form pseudohalogens. E. g. CN^-.

PSEUDOHALIDE AND PSEUDOHALOGEN

PSEUDOHALIDE-

Univalent negative inorganic radicals composed of two or more electronegative atoms, which shows similar reaction to those of the halide ions.$(X)^-$

E.G. – CN^-, SCN^-, N_3^-

PSEUDOHALOGEN

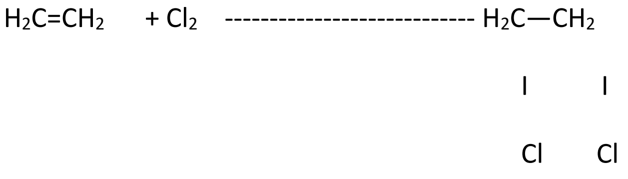
Dimer of pseudohalogens is called pseudo halogens. They show similar chemical properties with halogens. Example – $(CN)_2$, $(SCN)_2$,

SIMILARTIES WITH HALOGENS AND PSEUDOHALOGENS

1. Like halogens pseudohalogens are also dimeric in nature and fairly volatile in the free state.

2. pseudohalogens are isomorphous with halogens. Example $(CN)_2$ is isomorphous to Cl_2.

3.Pseudohalogens are added to ethylene double bond like ethylene double bond.



$$H_2C{=}CH_2 \quad + Cl_2 \quad \text{----------------------------} \; \underset{\displaystyle Cl}{\underset{|}{H_2C}}—\underset{\displaystyle Cl}{\underset{|}{CH_2}}$$

4. They show same reaction with alkali for example-

(i) $(SCN)_2$ + 2 KOH (COLD AND DILUTE) ----------- KSCN + KOSCN + H_2O

Cl_2 + 2 KOH ----------------- KCl + KOCl +H_2O

(ii) $3(SCN)_2$ + 6 KOH (HOT AND CONC.) ----------------- 5KSCN + $KSCNO_2$ + $3H_2O$

$3Cl_2$ + 6KOH (HOT AND CONC.) --------------- 5 KCl + $KClO_3$ + $3H_2O$

5. MONOBASIC HYDRACIDS

Pseudohalogens are also combine with H_2 to form monobasic hydracids like halogens.

Cl_2 + H_2 ----------------- 2 $HCl(CN)_2$ + H_2 ------------ 2HCN

6. Pseudohalogens and halogens show similar reaction with metals, for example with lead and mercury to form insoluble salts AgCN, Pb $(SCN)_2$

Ag^+ + Cl^- ------------- AgCl,

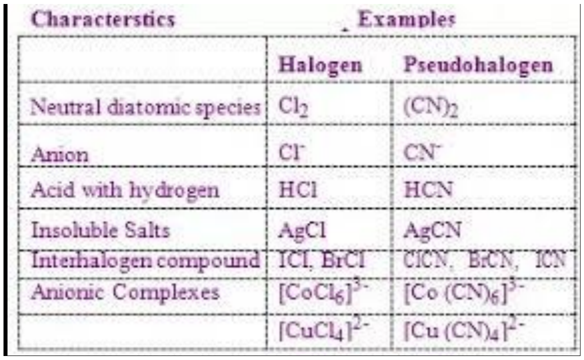
Ag^+ + CN^- --------------- AgCN

7. FORMATION OF MONOBASIC ACIDS

With hydrogen theh form monobasic hydracids.

Cl_2 + H_2 ------------ 2HCl

$(CN)_2$ H_2 ----------- 2HCN



Characterstics	Examples	
	Halogen	Pseudohalogen
Neutral diatomic species	Cl_2	$(CN)_2$
Anion	Cl^-	CN^-
Acid with hydrogen	HCl	HCN
Insoluble Salts	AgCl	AgCN
Interhalogen compound	ICl, BrCl	ClCN, BrCN, ICN
Anionic Complexes	$[CoCl_6]^{3-}$	$[Co\,(CN)_6]^{3-}$
	$[CuCl_4]^{2-}$	$[Cu\,(CN)_4]^{2-}$

Examples of symmetrical pseudohalogens (*Ps*–*Ps*)
include cyanogen $(CN)_2$, thiocyanogen $(SCN)_2$, selenorhodane $(SeCN)_2$, azidodithiocarbonate $(N_3CS_2)_2$. Another complex symmetrical pseudohalogen is dicobalt octacarbonyl, $Co_2(CO)_8$. This substance can be considered as a dimer of the hypothetical cobalt tetracarbonyl, $Co(CO)_4$.

Examples of non-symmetrical pseudohalogens (*Ps*–X), analogous to the binary interhalogen compounds, are cyanogen halides (ICN, ClCN, BrCN), and other compounds. Sometimes nitrosyl chloride NOCl also is considered as pseudohalogen.

INTERNALHALOGEN COMPOUND (STRUCTURE AND REACTION)

Interhalogen compounds are formed when two or more halogens connected with each-other through bond.

Less electronegative atom is central atom and having positive oxidation state. General principle of oxidation state is that – odd numbered group exhibit odd oxidation state, while even numbered group exhibit even number oxidation state.

CLASSIFICATION

Interhalogens have general formula AXn , where n is equal to – 1,3,5,7

AX- ClF, BrF, BrCl, ICl, IBr

AX3- ClF3, BrF3, ICl3

AX5- BrF5 , ClF5

AX7- IF7

THE LESS ELECTRONEGATIVE ATOM IS WRITTEN FIRST IN REPRESENTATION.

STRUCTURE-

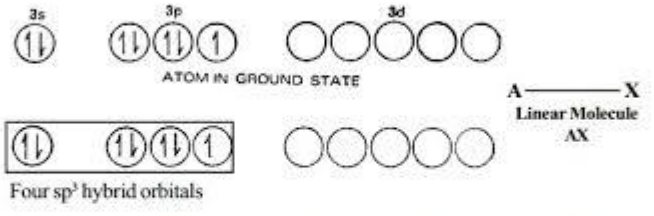


Figure Linear structure of the interhalogen compounds of the type AX

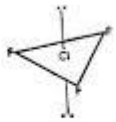


Fig. Bi pyramidal structure of ClF$_3$ molecule

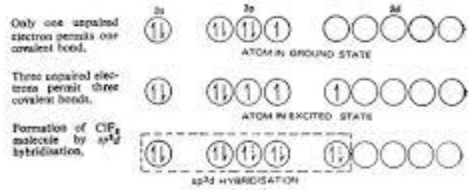
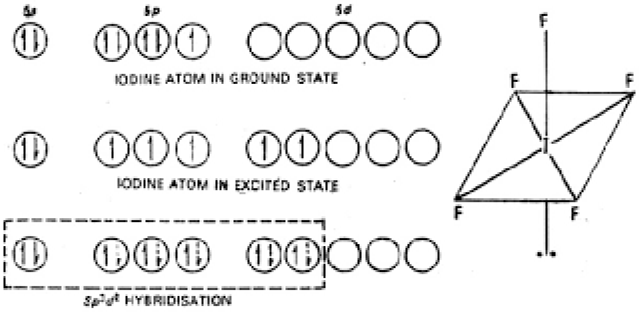


Fig. sp^3d hybridisation involved in the formation of Cl F$_3$ molecule



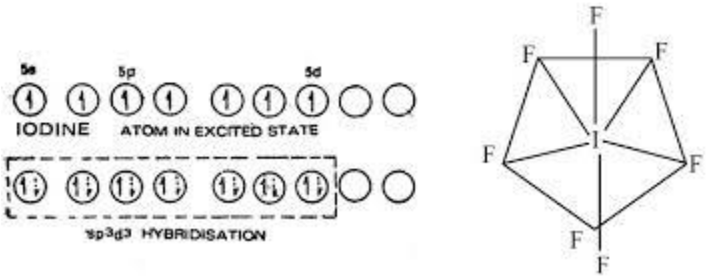
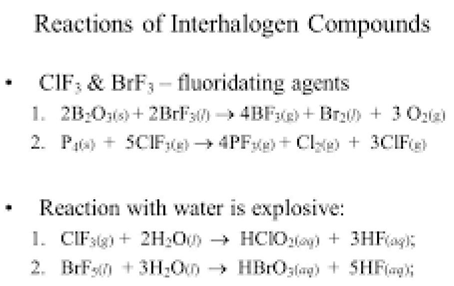


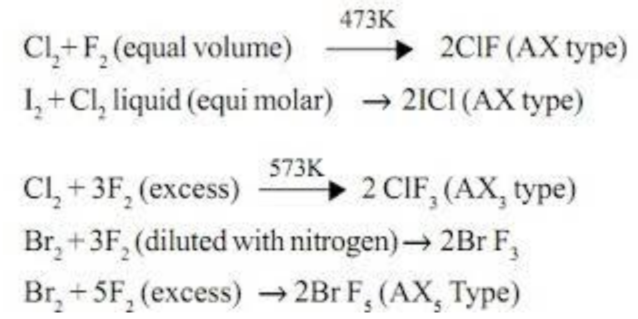
Figure pentagonal bipyramidal structure of AX7



Reactions of Interhalogen Compounds

- ClF_3 & BrF_3 – fluoridating agents
  1. $2B_2O_{3(s)} + 2BrF_{3(l)} \rightarrow 4BF_{3(g)} + Br_{2(l)} + 3\,O_{2(g)}$
  2. $P_{4(s)} + 5ClF_{3(g)} \rightarrow 4PF_{3(g)} + Cl_{2(g)} + 3ClF_{(g)}$

- Reaction with water is explosive:
  1. $ClF_{3(g)} + 2H_2O_{(l)} \rightarrow HClO_{2(aq)} + 3HF_{(aq)}$;
  2. $BrF_{5(l)} + 3H_2O_{(l)} \rightarrow HBrO_{3(aq)} + 5HF_{(aq)}$;



$Cl_2 + F_2$ (equal volume) $\xrightarrow{473K}$ $2ClF$ (AX type)

$I_2 + Cl_2$ liquid (equi molar) $\rightarrow 2ICl$ (AX type)

$Cl_2 + 3F_2$ (excess) $\xrightarrow{573K}$ $2\,ClF_3$ (AX_3 type)

$Br_2 + 3F_2$ (diluted with nitrogen) $\rightarrow 2Br\,F_3$

$Br_2 + 5F_2$ (excess) $\rightarrow 2Br\,F_5$ (AX_5 Type)

COMMON PROPERTIES OF HALOGEN GROUP-

IONISATION ENERGY

ELECTRON AFFINITY

ELECTRONEGATIVITY

OXIDISING STATE

OXIDISING POWER

IONISATION ENERGY OR IONISATION POTENTIAL (IE OR IP)

IP is knowmn as the amount of energy required for the removal of valence electron from valence cell of isolated gaseous atom to form cation.

So the ionization energy is depend on the attraction between outermost electron and nucleus. As moving down in a group the distance between the valence electron and nu cleus increase , the attraction between them are also decreases and less amount of energy is required to remove the electron from the shell. More over the shielding effects also works here, so the less amount of energy is required to remove the electron is required as we go down to the group. Iodine lose an e- easily and form cation and display metallic character.

So in halogen IP decreases in a group. F shows highest IP in the group.

ELECTRONEGATIVITY (DECREASES DOWN IN THE GROUP)

It is a measure of tendency to attract the bondinng pair of electron of sigma bond towards itself.

As moving down in a group the distance of e- from nucleus increases and also due to shielding effect electron egativity decreases down the group. F is most electronegative element in pereiodic table. Electronegativity decreases down in the group.

OXIDISING STATE

All halogens show -1 oxidation state. Accept F ,other halogens shows positive oxidation state.

HALOGEN	OXIDATION STATE
F	-1
Cl	-1,+1,+3
Br	-1,+1,+3,+5
I	-1,+1,+3,+5,+7

OXIDISING POWER

Halogens are strong oxidizing agent.

Fluorin is strongest oxidizing agen, oxidizing power decrease in a group.fluorine oxidize other halogens also.

$F_2 + 2X^- \text{-----------} 2F^- + X_2$ (X=Cl,Br,I)

The reactivity of the halogens decreases down in the group.

Electron affinity decreases down in the group. But due to small size of fluorine the electron affinity of Cl is greater than F.

ABNORMAL BEHAVIOR OF "F"

F differs from other family members. The following point are responsible for the abnormal behavior of F

- Small Size
- High Electronegativity
- Non availability of d orbitals.

Hydrogen fluoride has high melting point and boiling point than other hydrogen halide, this is due to hydrogen bonding. Due the difference in electronegativity hydrogen fluoride make interhydrogen bond which is responsible for high M.P & B. P. , and this is the reason why hydrogen fluoride is liquid.

H-F ------------ H-F------------H-F

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