B] Chemistry of Halogen Compound

a) **Inter-halogen compounds :-**

Each halogen combines with every other halogen to form compounds amongst themselves. These compounds are known as interhalogens or interhalogen compounds.

The less electro-ve halogen is written first.

Interhalogens are divided in to two categories.

1) Neutral ~~mole~~ Interhalogen

2) cationic or anionic interhalogens

(1) **Neutral interhalogens :-**

These are divided into four types as ~~AX, AX3~~ XY, XY_3, XY_5, XY_7

XY	XY_3	XY_5	XY_7
- ClF	ClF_3	BrF_5	IF_7
Chlorine fluride	Chlorine trifluoride	bromine Pentafluoride	Iodine hepta fluoride
- BrF	BrF_3	IF_5	
bromine fluoride			
- IF	ICl_3		
- BrCl			
- ICl			
- IBr			

① Interhalogens of the type XY

Preph :- All the compounds of this type are made by direct combination of the constituent halogens

$Cl_2 + F_2 \xrightarrow{250^\circ C} 2ClF$. (colourless gas)

$I_2 + F_2 \xrightarrow{-45} 2IF$.

$I_2 + X_2 \longrightarrow 2IX$.

other method ⇒ $Cl_2 + ClF_3 \xrightarrow{300^\circ C} 3ClF$

$I_2 + AgF \xrightarrow{0^\circ C} IF + AgI$.

Properties :- Interhalogens of type XY are essentially covalent compounds because of small diff in electro-vity

- they differ in thermal stabilities.

e.g. ✓ ClF is extremely stable.

✓ ICl & IBr are moderate stable while BrCl is unstable

- ClF is used to fluorinate many metals & non metals

$6ClF + 2Al \longrightarrow 2AlF_3 + 3Cl_2$

$6ClF + S \longrightarrow SF_6 + 3Cl_2$.

- ICl is used as Wij's reagent for the estimation of the iodine number of fats & oils.

Structure :- XY type involve sp^3 hybridisation & have linear shape

Cl in G.S. : 1↓ | 1↓ | 1↓ 1 | | | | | |

$3s^2$ — $3p^5$

In covalent bond formed : 1↓ | 1↓ | 1↓ 1↓ 1↑ — sp^3

Cl.

X — Y

(11) Interhalogens of type XY_3.

In this 3 atoms of one halogen combine with one atom of another halogen. e.g. ClF_3, BrF_3, ICl_3

These are generally prepared by the direct combination of the elements under suitable condn. are chosen with the care.

e.g. $Cl_2 + 3F_2 \xrightarrow{200-300} 2ClF_3$.

$ClF + F_2 \xrightarrow{200-300°C} ClF_3$.

$Br_2 + 3F_2 \longrightarrow 2BrF_3$; $ClF_3 + Br_2 \longrightarrow BrF_3 + BrCl$

$I_2 + 3xeF_2 \longrightarrow 2IF_3 + 3Xe$

$I_2 + 3Cl_2 \longrightarrow 2ICl_3$, ; $ICl + Cl_2 \longrightarrow ICl_3$.

$I_2O_5 + 10HCl \longrightarrow 2ICl_3 + 5H_2O + 2Cl_2$

Properties – ClF_3 is one of the most reactive compounds

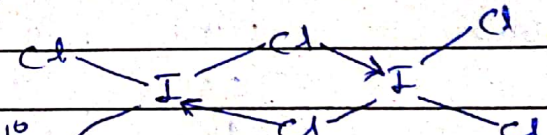
– It catches fire spontaneously with wood & most building material.

– It was used in incendiary bombs in world-war-II

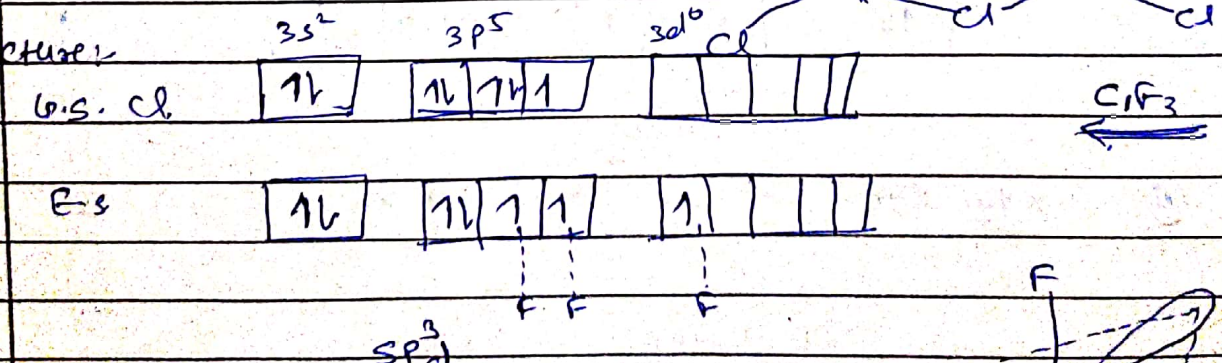
– It is used in nuclear industry for fuel processing.

– It is used to fluorinate organic compounds.

– All interhalogens of this type acts as Potential non-aqueous ionising solvents. – ICl_3 does not exist, but the dimer I_2Cl_2 is bright yellow solid



Structure:



③ XY_5 type

Three comp. of this category are known. i.e. ClF_5, BrF_5 & IF_5

Prep^n: these comp. are prepared by direct fluorination of the element.

$$Br_2 + 5F_2 \xrightarrow{150^\circ C} 2BrF_5$$

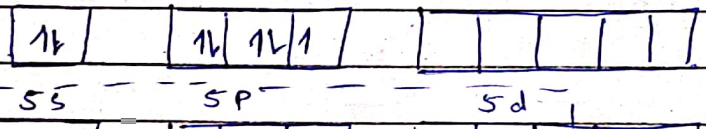
$$Cl_2 + 5F_2 \xrightarrow[200\,atm]{350^\circ C} 2ClF_5 \quad \text{or} \quad ClF_3 + F_2 \xrightarrow{h\nu} ClF_5$$

$$I_2 + 5F_2 \xrightarrow{20^\circ} 2IF_5$$

Prop.:
- ClF_5 is extremely vigorous fluorinating agent.
- BrF_5 is highly reactive & react very violently.
- It is used in org. synthesis as an oxidiser for propellent.

Str.: XY_5 interhalogens involve sp^3d^2 hybri & square py str.

G.S



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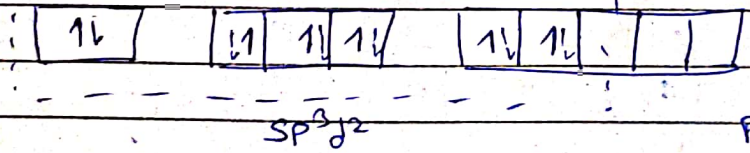
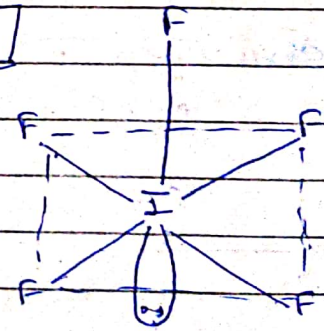




④ XY_7 type - IF_7 is the only cx.

Prep^n.

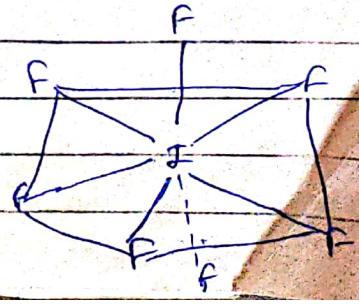
$$IF_5 + F_2 \longrightarrow IF_7$$

$$KI + 4F_2 \longrightarrow IF_7 + KF$$

$$PdI_2 + 8F_2 \longrightarrow 2IF_7 + PdF_2$$

Prop. it is violent fluorinating agent

Str. Hybri. = sp^3d^3 geometry Pentagonal Bipyramidal



Pseudohalides & Pseudohalogenes:

Pseudohalides: There are several uni-negative groups that show similar properties as that of halide ions. These uni-ve gr. are called Pseudohalides. It contains two or more atoms of which at least one is nitrogen.

Pseudohalogens: As each halide ion has a corresponding halogen (Cl^- For eg. has Cl_2 as the corresponding halogen) Few Pseudohalide ions have their corresponding covalent dimer called as Pseudohalogen.

So far only Four Pseudohalogens which are covalent dimers of the Pseudohalide ions have been isolated.

Pseudohalide ions	Formulae		Pseudohalogens	formula
cyanide	CN^-	—	Cyanogen	$(CN)_2$
Cyanate	OCN^-			
Thiocyanate	SCN^-	—	Thiocyanogen	$(SCN)_2$
Selenocyanate	$SeCN^-$	—	seleno Cyanogen	$(SeCN)_2$
Azide	N_3^-			
Azidothiocarbonate	$SCSN_3^-$	—	Azidocarbon disulfide	$(SCSN)_2$
isocyanate	ONC^-			

1) Cyanogen $(CN)_2$

- It is obtained by heating AgCN

1) $2AgCN \xrightarrow{\Delta} 2Ag + (CN)_2$

2) $Hg(CN)_2 + HgCl_2 \longrightarrow Hg_2Cl_2 + (CN)_2$

3) $CuSO_4 + 4KCN \xrightarrow{60^\circ C} (CN)_2 + 2CuCN + K_2SO_4$

Properties :
- It is colourless gas
- soluble in water & poisonous in nature
- on cooling, it condenses to a liq. at $-21.2^\circ C$ & freezes at $-27.9^\circ C$
- when heated, it polymerises to give insoluble paracyanogen $(CN)_n$.
- It is fairly stable in water but it's alkaline soln decomposes to give CN^-, & OCN^- ions

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2) Thiocyanogen $(SCN)_2$

Prepn : 1) $2AgSCN + Br_2 \longrightarrow 2AgBr + (SCN)_2$
silver sulphocyanide

Prop :
- It is yellow solid.
- It polymerises irreversibly at room temp. to give a brick-red material, Insoluble in H_2O
- It oxidises iodides to iodine, $Cu^+ \rightarrow Cu^{2+}$ & H_2S to sulphur

$(SCN)_2 + 2KI \longrightarrow 2KSCN + I_2$

$(SCN)_2 + 2CuSCN \longrightarrow 2Cu^{2+} + 4(SCN)^-$

$(SCN)_2 + H_2S \longrightarrow 2H^+ + S + 2(SCN)^-$

Selenocyanogen $(SeCN)_2$

Prepn
1) $Pb(SeCN)_4 \xrightarrow{\Delta} Pb(SeCN)_2 + (SeCN)_2$

2) $2AgSeCN + I_2 \longrightarrow 2AgI + (SeCN)_2$

Prop :
- It is a yellow crystalline substance which turns red on standing.
- It is quite stable when dry but reacts with water as

$2(SeCN)_2 + 3H_2O \longrightarrow H_2SeO_3 + 3HSeCN + HCN$

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4) Azidocarbondisulphide $(SCSN_3)_2$

$CS_2 + KN_3 \xrightarrow{40^\circ C} KSCSN_3 \xrightarrow{H_2O} (SCSN)_2$

- It is not a stable compound as it decomposes even at R.T. in accordance with the eqn

$(SCSN_3)_2 \longrightarrow 2N_2 + 2S + (SCN)_2$

Prop:- These have close resemblance with the Prop. of

1) Pseudohalogens are volatile like halogens

2) Pseudohalides ions like halide ions combine with hydrogen to give acids, which are usually weak.

3) P. halogens, like halogens add across double & triple C-C bonds.

$$CH_2=CH_2 + (SCN)_2 \longrightarrow \underset{SCN}{CH_2}-\underset{SCN}{CH_2}$$

(4) P. halogens like halogens reacts with alkalies

$$(SCN)_2 + 2KOH \longrightarrow KSCN + KSCNO + H_2O$$

$$3(SCN)_2 + 6KOH \longrightarrow 5KSCN + K(SCN)O_3 + 3H_2O$$

(5) P. halides ions, like halide ions combine with Ag^+ & Pb^{2+} to form ppt of low solubility.

(6) P. halides form several complexes

e.g. $[Co(SCN)_4]^{2-}$ & $[Hg(CN)_4]^{2-}$. The corresponding halide complexes are $[CoCl_4]^-$ & $[HgI_4]^{2-}$

Fluorocarbons

Fluorocarbons are hydrocarbons or other organic molecules in which most of the hydrogen atoms are replaced by Fluorine.

1) By heating metal fluorides (MF_x) such as LiF, NaF, CsF, HgF_2, ZnF_2, SbF_3 etc with organic halides

$$RCl + MF \longrightarrow RF + MCl.$$

Fluoro carbon

2) By electrolysing organic comp. in liq. HF in steel cells with Ni anode & steel cathode.

$$C_8H_{18} \xrightarrow[\text{liq. HF}]{\text{electrolysis}} C_8F_{18}$$

$$(C_4H_9)_3N \xrightarrow[\text{liq. HF}]{} (C_4F_9)N.$$

3) $2CCl_4 + 3HF \xrightarrow[50-100^\circ C,\ 5\text{ atm}]{SbF_5} CCl_2F_2 + CCl_3F + 3HCl$

4) $C_6H_6 + 9F_2 \xrightarrow[N_2 \text{ or } He]{Cu \text{ at } 265^\circ C} C_6F_{12} + 6HF$

5) $\begin{matrix} R \\ R \end{matrix}\!\!>\!CO + SF_4 \longrightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!CF_2 + SOF_2$

Properties:- 1) Since bond energy of C-F bond (486 KJ/mol) is very high compared to the bond energies of C-H bond (415 KJ/mol) & C-Cl bond (332 KJ/mol), Fluorocarbons are highly stable compounds.

2) Fluorocarbons are stable towards hydrolysis (since no d-orbital)

3) F has small size ∴ replacement of H by F atoms does not produces any appreciable strain in the molecule ∴ stable.

4) Fluorocarbons are not very reactive. This is due to F-atoms shields the carbon very effectively.

5) Fluorocarbons are not attacked by acids, alkalies & most other chemicals. They are attacked only by hot metals such as molten sodium.

6) completely fluorinated compounds have very low boiling points. due to weak intermolecular forces.

Uses: 1) Fluorocarbons are used as lubricants because of their very low coefficient of friction.

2) CFC such as CCl_3F, $CClF_3$, CF_2Cl_2 are used as refrigerants

3) $CF_3CHBrCl$ & some halothane comp. are used as anaesthetics

4) certain Perfluoro organics are used as 'synthetic blood' for small mammals. These are non-toxic & have capacity to dissolve transport & release oxygen by simple solubility.

5) $CHClF_2$ is used for Preparing tetrafluoro ethylene which further converted into teflon by polymerisation

$$2\,CHClF_2 \xrightarrow{500-1000^\circ C} CF_2=CF_2 + 2HCl$$

$$n\,CF_2=CF_2 \xrightarrow{\text{Polymerisation}} -(CF_2-CF_2)_n-$$

Poly halides ⟹ There are large number of interhalogen & Polyhalogen anions & cations are known

e.g. Triatomic anion - ICl_2^-, IBr_2^-, $BrCl_2^-$, ClF_2^-, $IBrCl^-$, I_3^-

Pentaatomic anion - ICl_4^-, BrF_4^-, I_5^+

Types: Hetero Poly halogen $[ClF_2]^+$, $Cl_2F]^+$

isoPoly halo - $[Cl_3]^-$, Br_3^-

Interhalogen Anions :-

In general for a given cation, symmetrical interhalogen anions are more stable than the unsymmetrical ones. stability also increases with increasing size of the central atom.

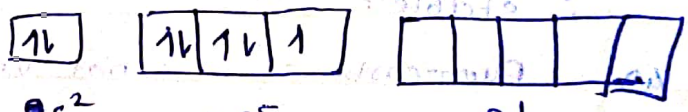
Str. of the interhalogen is established by X-ray measurement.

(1) Str. of ICl_2^- Iodine dichloride anion.

$KI + Cl_2 \longrightarrow K^+[ICl_2]^-$

$KI + ICl_3 \longrightarrow K^+[ICl_4]^-$

G.S. I

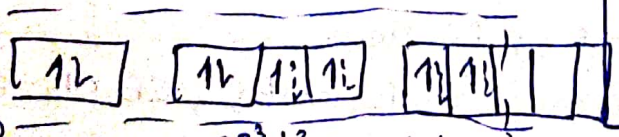


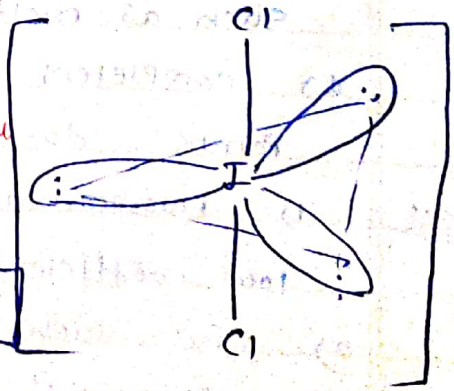
G.S. I^-

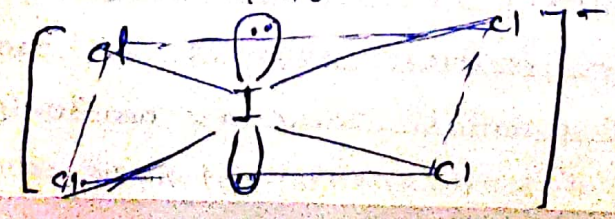
= Linear str. of ICl_2 ion involving sp^3d hybrid. of I^- orbitals

(2) ICl_4^- Geometry - tri-angular bipyramidal

E.S. I







Oxides of halogens

- All the halogens form oxides. Twelve such oxides are known
- The oxides of Fluorine are considered as oxygen Fluoride.
- most of these oxides are unstable & liable to explode.
- All the oxides of halogens are Powerful oxidising agent.

of F2

(1) oxide of fluorine :-

Difluorine oxide F_2O ;

Prepⁿ : $2NaOH + 2F_2 \longrightarrow F_2O + 2NaF + H_2O$.

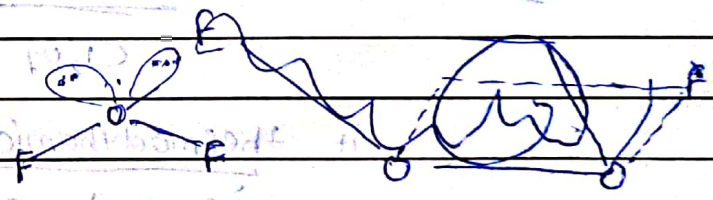
- It is a Pale yellow gas which is highly poisonous.
- It decomposes in the presence of water to yield HF.

$$H_2O + F_2O \longrightarrow 2HF + O_2$$

- F_2O used as rocket fuel.

Str :-

- The orbitals of central oxygen atom are sp^3 hybridised.
- Two of the sp^3 hybrid orbitals are occupied by lone pair of e⁻ & the other two involved in σ-bonding with two F atoms
- The FoF angle is 103°C.



(2) oxides of Chlorine :-

Cl forms number of oxides such as Cl_2O, ClO_2, Cl_2O_6, & Cl_2O_7. — All are unstable & highly reactive.

(A) Cl_2O (Dichlorine oxide) $2Cl_2 + 2HgO \longrightarrow HgO.HgCl_2 + F_2O$

Prop: It is orange liquid below 2°C.

It boils at 2°C to give Yellowish brown gas.

At higher temp the gas explodes.

- It undergoes Photochemical decomposition giving O & Cl.

$$2Cl_2O + h\nu \longrightarrow 2Cl_2 + O_2$$

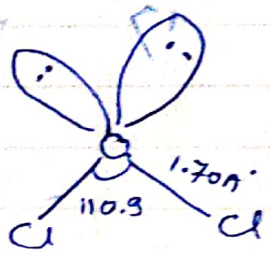
- It dissolves in water to form hypochlorous acid with which it exist in equilibrium in aq. soln.

$$Cl_2O + H_2O \rightleftharpoons 2HOCl.$$

- Cl_2O is, therefore regarded as the anhydride of hypochlorous acid.
- Its gaseous mix. with NH_3 explodes violently.

$$3Cl_2O + 10NH_3 \longrightarrow 2N_2 + 6NH_4Cl + 3H_2O$$

Structure → - Cl_2O has an angular str.



- The Cl-O-Cl bond angle is 110.9°
- O-Cl bond length 1.70Å
- oxygen orbitals are sp^3 hybridised.
- Two of the four sp^3 hybrid orbital are occupied by lone pairs of $\bar{e}$ & the remaining two are used in forming σ-bonds with 2 Cl atoms

Prep^n

① $2AgClO_3 + Cl_2 \xrightarrow{90^\circ C} 2AgCl + 2ClO_2 + O_2$ (Silver chlorate)

② $2NaClO_2 + Cl_2 \longrightarrow 2ClO_2 + 2NaCl$ (Sod. chlorite) (X)

(B) Dichlorine heptoxide: Cl_2O_7.

Prep^n Eg: It is obtained by dehydrating Perchloric acid with P_2O_5

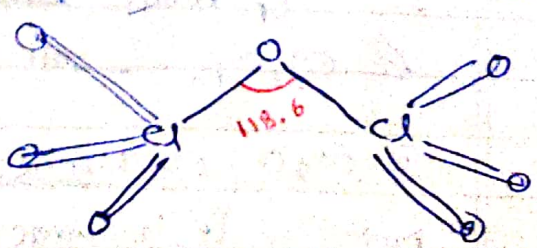
$$2HClO_4 \xrightarrow{P_2O_5} Cl_2O_7 + H_2O$$

Prop^n; It is colourless oily liq. & dissolves in H_2O giving Perchloric acid

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

- It thermodynamically more stable than any other oxide of Cl
- It is not strong o.A.
- It is less reactive than the lower oxides of Cl.

Str^e:



- ClO_2 is evolved as a paramagnetic yellowish-green gas which on condensation gives colored liq. (b.p. 11°C) - It is powerful O.A. & Chlorinating agent - It dissolves in water exothermically. (6)

(c) I_2O_5 :-

Prep^n : it is prepared by heating iodic acid to about 240°C.

1) $2HIO_3 \xrightarrow{240°C} I_2O_5 + H_2O$

or

2) $I_2 + 10HNO_3 \longrightarrow I_2O_5 + 10NO_2 + 5H_2O$

Prop :

1) It is a white solid which decomposes to iodine & O above 300°C

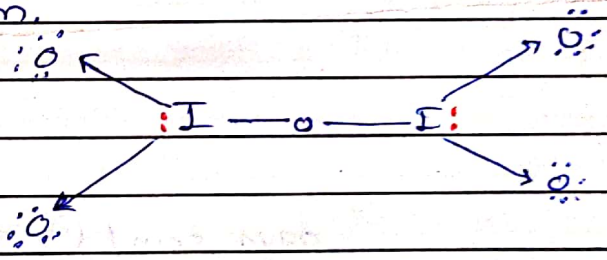
2) with water it forms iodic acid HIO_3

3) It is strong O.A.

4) I_2O_5 is used for the detection & estimation of CO.

Str : The str. of I_2O_5 has been determined from IR.

- It has two Pyramidal IO_3 units joined through a common oxygen atom.



5) It oxidises CO to CO_2 quantitatively liberating iodine which can be titrated against sod. thiosulphate

$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$

Hence I_2O_5 is used for detection & estimation of carbon monoxide.

Relative strength of oxoacids of Halogen =

Oxyacids of halogens

- The oxyacids of Cl & I, particularly containing more oxygen are more stable & known in pure state. This is due to increase in the oxidn state of halogen from +1 to +7
- e.g. $HClO_4$, HIO_3, HIO_4 (meta periodic acid), H_5IO_6 (para periodic acid)
- oxoacids of bromine are known only in soln or in the form of their salts.

e.g. $HBrO_3$ (in soln), $HBrO_2$ (in salts) but $HBrO_4$ is unknown.

- Fluorine does not form oxoacids. This is due to F is more electro-ve than oxygen.

Strength

The strength of oxoacids in which the halogen are in the same oxidn state, generally decreases with rise in at. no. of halogen. Thus $HClO_3$ is strongest while HIO_3 is the weakest of all the oxoacids in which oxidn state of halogen is +5.

Structure:- The halate ion (ClO_3^-, BrO_3^- or IO_3^-) is formed by the sp^3-hybridisation & has a pyramidal str.

type	oxidn state	oxoacids of Cl	oxoacids of Br	oxoacids of I
HXO	+1	$HClO$	$HBrO$	HIO
HXO_2	+3	$HClO_2$		
HXO_3	+5	$HClO_3$	$HBrO_3$	HIO_3
HXO_4	+7	$HClO_4$	$HBrO_4$	HIO_3

decreases →

Stability ↓ decreases

Acid strength ↓ decreases

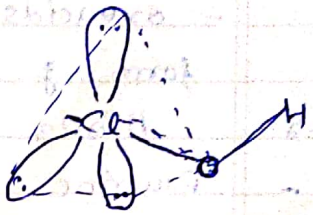
Properties

① HOX - (Hypohalous acids)

+1

- HOF is colourless gas
- HOX comp. are also unstable
- They are known only in soln. from the interaction of halogen & Hg^{II} oxide
- The hypohalous acids are very weak acids but good oxidising agents.

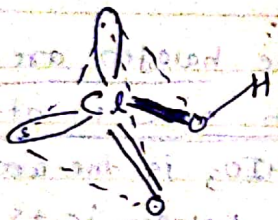
Str



② HXO_2 (Halous acid)

+3

- The only halous acid known is chlorous acid $HClO_2$.
- It only exist in soln
- It is a weak acid but stronger than HOCl.
- salts of $HClO_2$ are called chlorites.
- chlorites are used as bleaches.



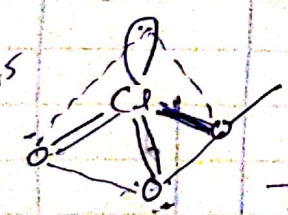
$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_2 + H_2O$$

③ HXO_3 (Halic acid) - $HClO_3$, $HBrO_3$, HIO_3 are known

Iodic acid HIO_3 is stable, white solid obtained by oxidising I_2 with conc HNO_3, H_2O_2, O_3 & so on.

- The halic acids are strong acids & are powerful oxidising agents
- The salts of $HClO_3$ are called chlorates.

+5



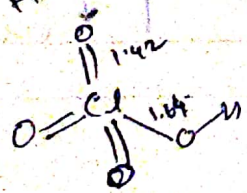
$$6NaOH + 3Cl_2 \xrightarrow{80^\circ C} NaClO_3 + 5NaCl + 3H_2O$$

- Uses
  - To make fireworks & matches
  - Solid chlorates, bromates & Iodates should be handeld carefully
  - Chlorate can explode on grinding or on heating
  - Solid sod. chlorate has been used by terrorist to make bombs

④ HXO_4 (Perhalic acid)

+7

- Perbromic - colourless
- $HClO_4$ - strongest acid.



ClO_4^- is weak lewis base with little tendancy to form complexes with cation in aq soln