NARAYANA IIT ACADEMY INDIA
40 YEARS OF EXCELLENCE

BASARA SARASWATHI BHAVAN_MDP N-120

Section: Senior **Date: 18-06-2020**
Name of the student: **Group-17** **I.D.No:** **Sec:**

Property	
Elements & Physical state	F_2(gas) Cl_2(gas) Br_2(liquid) I_2(solid)
General electronic configuration	$ns^2\ np^5$
Oxidation states	Possible oxidation states are – 1 + 1 + 3 + 5 and + 7, 'F' always exhibits –1 other elements exhibit –1 with less E.N elements. Cl, Br, I can exhibit positive states if combines with more E.N. elements.
Valency	Variable valancies are 1, 3, 5, 7. Fluorine is always monovalent can't expand valancy due to lack of vacant 'd' orbitals.
Colour	Colour due to absorption of certain wave length of visible light resulting from excitation of outer $\bar{e}$ to higher energy level F_2 (light yellow) Cl_2 (yellow green) Br_2 (dark reddish brown) I_2(violet) → aqueous solution of I_2 brown in colour I_2(violet) → organic solution violet in colour I_2 (solid) conducts electricity to small extent (intrinsic semiconductor) $I_{2(liquid)}$ conducts very slightly due to self ionization ($I_2 \rightleftharpoons I_3^+ + I_3^-$) $\left.\begin{array}{l} Cl_2(water) \xrightarrow[evaporation]{careful} Cl_2.8H_2O \\ Br_2(water) \longrightarrow Br_2.8H_2O \end{array}\right\}$ crystals
Bond energy	Expected to decrease from F_2 to I_2. But bond energy of F_2 less than Cl_2 and Br_2 due to small size and electron – electron repulsion. $Cl_2 > Br_2 > F_2 > I_2$.
E.A	$F_2 < Cl_2$ due to extremely small size and electron – electron repulsion in

	fluorine. The order of E.A is: $Cl > F > Br > I$
S.R.P values (E^0)	F(2.8) Cl(1.36) Br(1.08) I(0.54) As SRP values decreases oxidising capacity also decreases.

SRP values depend on several factors.

$$\frac{1}{2}X_{2\,(Solid)} \xrightarrow{\Delta H_f} \frac{1}{2}X_{2\,(liquid)} \xrightarrow{\Delta H_{vap}} \frac{1}{2}X_{2\,(gas)}$$

$$\downarrow \Delta H\ dis$$

$$X^-\left(H_2O\right)_n \xleftarrow[H.E]{H_2O} X^-_{(g)} \xleftarrow[E.A]{+1e} X(g)$$

Net energy required for oxidising reaction = $\frac{1}{2}\Delta H_f + \frac{1}{2}\Delta H_{vap} + \frac{1}{2}B.D.E + E.A + H.E$.

- For I_2 ΔH_f and ΔH_{vap} are added $\therefore$ have low value of SRP.
- High hydration of F^- compensates electron affinity

$\therefore$ F_2 is strongest oxidising agent.

Displacement reaction:

More oxidising halogen liberates less oxidising halogen from its halide.

$$2NaX + F_2 \longrightarrow X_2 + 2NaF$$

X = Cl, Br,I.

Or

$$2X^- + F_2 \longrightarrow X_2 + 2F^-$$

But I_2 can liberate Br_2 and Cl_2 from their oxo acids and salts

eg. $2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$

$2KBrO_3 + I_2 \longrightarrow 2KIO_3 + Br_2$

Chemical reactivity:

F_2 most reactive. Reactivity decreases down the group.

Reaction with water:

$$2F_2 + 2H_2O \xrightarrow{Cold} 4HF + O_2$$

$$2F_2 + 3H_2O \xrightarrow{Hot} 6HF + O_3$$

Cl_2 & Br_2 can disproportionate H_2O in presence of light

$$X_2 + H_2O \longrightarrow HX + HOX$$

(X = Cl, Br)

I_2 does not react with water (insoluble) but dissolves in water in presence of I^- due to formation of I_3^-.

Reaction with base:

$$F_2 + \underset{\substack{(Cold)\\ Dilute}}{NaOH} \longrightarrow NaF + H_2O + OF_2$$

$$F_2 + \underset{\substack{(Hot)\\ Conc}}{NaOH} \longrightarrow NaF + H_2O + O_2$$

Other halogen X_2 (Cl_2, Br_2 & I_2) disproportionate

$$X_2 + \underset{\substack{Cold\\ Dilute}}{NaOH} \longrightarrow NaX + H_2O + \underset{hypohalite}{NaXO}$$

$$X_2 + \underset{\substack{hot\\ Conc}}{NaOH} \longrightarrow NaX + H_2O + \underset{halite}{NaXO_3}$$

Reduction with $Na_2S_2O_3$:

$$Cl_2 + H_2O + Na_2S_2O_3 \longrightarrow NaHSO_4 + HCl$$

$$Br_2 + H_2O + Na_2S_2O_3 \longrightarrow NaHSO_4 + HBr$$

$$Na_2SO_4 + NaI \xleftarrow{OH^-} \boxed{Na_2S_2O_3} + I_2 \xrightarrow{H^+} Na_2S_4O_6 + NaI$$

Reaction with NH_3:

$$F_2 + NH_3 \longrightarrow NF_3 + HF$$

$$Cl_2 + \underset{(excess)}{NH_3} \longrightarrow NH_4Cl + N_2$$

$$\underset{(excess)}{Cl_2} + NH_3 \longrightarrow NCl_3 + HCl$$

Br_2 also reacts in the same way as Cl_2.

$$NH_3 + 3I_2 \xrightarrow[-3HI]{} NI_3.NH_3 \longrightarrow N_2 + I_2 + NH_4I\,.$$

OXIDES:

1. **Cl_2O (Chlorine Monoxide):** Yellow brown gas (used to bleach wood pulp and fabrics]

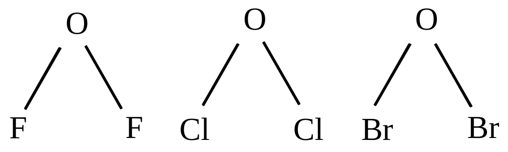
   Preparation: (Lab and industrial method) reaction of dry Cl_2 with HgO.

$$\underset{\substack{\text{diluted with}\\ \text{dry air}}}{Cl_2} + \underset{\substack{\text{Freshly}\\ \text{Precipitate}}}{HgO} \xrightarrow[\Delta]{} HgCl_2.HgO + Cl_2O$$

☞ Cl_2O explodes on heating or in presence of reducing agent like NH_3.

$$Cl_2O + NH_3 \rightarrow NH_4Cl + N_2 + H_2O$$

☞ **Structures of**: $OF_2, \mathbf{Cl_2O} \, \& \, \mathbf{Br_2O}$



Bond angles 103^0 111^0 $>111^0$

Expected bond angles based sp^3 hybridisation of central atom $109^0 28'$.

☞ In OF_2 'F' is more electro negative than oxygen so bond pairs lies very close to 'F'.

$\therefore$ lone pair – lone pair repulsion is more than bond pair – bond pair repulsion.

$\therefore$ bond angle is lesser than expected.

☞ In Cl_2O & Br_2O, 'O' being more electro negative than 'Cl' and 'Br' the bond pair lies close to oxygen atom.

$\therefore$ bond pair – bond pair repulsion is more than lone pair – lone pair repulsion.

$\therefore$ bond angle is more than expected.

☞ O_2F_2 is unstable and strong oxidising as well as fluorinating agent. The structure is similar to that of H_2O_2 but O – O – bond length is shorter (1.22A) than – O – O – that of H_2O_2 (1.48 A^0).

☞ The O – F bond length (1.58 A^0) in O_2F_2 is longer than that in OF_2.

☞ Cl_2O is dissolves in water to form hypochlorous acid.

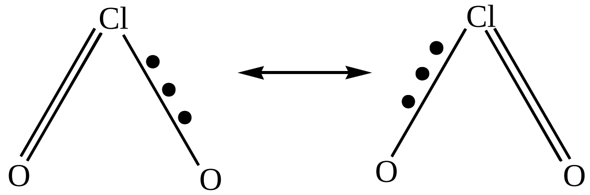
☞ $\therefore$ It is an anhydride of hypochlorous acid. So its reaction with base (NaOH) gives hypochlorite.

$$H_2O + Cl_2O \rightarrow HClO$$

$$Cl_2O + NaOH \rightarrow NaOCl + H_2O$$

2. **ClO_2 Chlorine dioxide:** (powerful oxidising and chlorinating gas)

Explodes at above – 40^0C at higher concentration and when mixed with reducing agents like NH_3.



☞ In ClO_2 the bond angle is 118^0C and the bond length is $1.47A^0$.

☞ It is an odd electron molecule so exhibits paramagnetism.

☞ Odd electron molecules generally dimerise. But ClO_2 does not as the odd electron bond is stabilized by resonance.

Preparation:

(i) $AgClO_3 + Cl_2 \rightarrow AgCl + ClO_2 + O_2$ (unsafe method)

As concentration of ClO_2 increases it leads to explosion.

(ii) $NaClO_3 + (COOH)_2 \rightarrow NaCl + (COONa)_2 + CO_2 + H_2O + ClO_2$ (safe method)

ClO_2 is diluted with CO_2 to prevent the explosion.

☞ Cl_2O is mixed anhydride of chlorous and chloric acid.

$$\underset{\text{(paramagnetic)}}{2ClO_2} + H_2O \longrightarrow HClO_3 + HClO_2$$

☞ So it react with base to generate

$$2ClO_2 + NaOH \rightarrow NaClO_3 + NaClO_2 + H_2O$$

3. BrO_2:

Preparation:

(i) By silent electric discharge of on Br_2 & O_2

(ii) Low temperature ozanalysis of Br_2

$$Br_2 + 6O_3 \rightarrow 2BrO_2 + 6O_2$$

BrO_2 + NaOH $\rightarrow$ NaBr + $NaBrO_3$ + H_2O.

4. Cl_2O_6: (dichlorine hexoxide) (dark red liquid)

Strong oxidising, dia magnetic

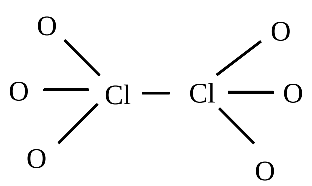
Preparation:

Ozonolysis of ClO_2

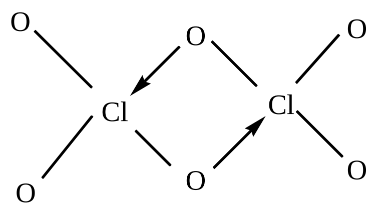
$$2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$$

Structure: Cl_2O_6 structure is known. The possible structures are given below.

Structure (i):



Structure (ii):



Ionic composition (solid state): $ClO_2^+ ClO_3^-$

☞ Cl_2O_6 is a mixed anhydride of chloric and perchloric acids.

$$\underset{\text{(dia magnetic)}}{Cl_2O_6} + H_2O \longrightarrow HClO_3 + HClO_4$$

☞ So it forms chlorate and perchlorate with base.

$Cl_2O_6 + NaOH \rightarrow NaClO_3 + NaClO_4 + H_2O$

5. **<u>Cl_2O_7:</u>** (dichlorine heptoxide)

- Explosive, colour less liquid.
- Only exothermic oxide of chlorine.

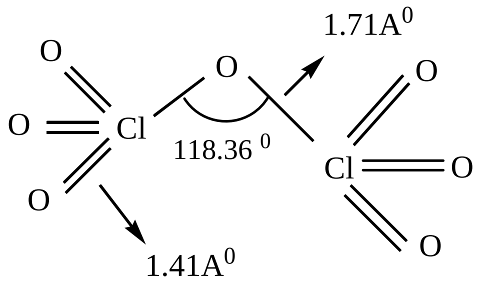
Preparation: Dydehydration of $HClO_4$.

$$2HClO_4 \xrightarrow[-H_2O,\ -10^0 C]{P_4O_{10}} Cl_2O_7.HPO_3$$

$$\because \left\{\begin{matrix} P_4O_{10} + H_2O \rightarrow H_3PO_4 \\ H_3PO_4 \xrightarrow[-H_2O]{P_4O_{10}} HPO_3 \end{matrix}\right\}$$

Structure:

Bent structure with bridging 'O' atom.



- It is a true anhydride of perchloric acid.

$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$

- So it forms perchlorate on reaction with base

$Cl_2O_7 + NaOH \longrightarrow NaClO_4 + H_2O$

- Cl_2O, ClO_2, ClO_3 (or) Cl_2O_6 & Cl_2O_7

Increasing order of acidic character due to increasing oxidation state of chlorine.

- Oxides with the same oxidation state.

$$\underset{\text{Oxides}}{Cl} > \underset{\text{Oxides}}{Br} > \underset{\text{Oxides}}{I}$$

Decreasing order of acidic character due to decreasing in non – metallic character.

<u>Oxides of iodine:</u>

(i) I_2O_5: Covalent

(ii) I_2O_4: ionic $\rightarrow IO^+ \ IO_3^-$

(iii) I_4O_9: ionic $\rightarrow I^{+3}\left(IO_3^-\right)_3$

(ii) and (iii) are less stable than I_2O_5.

<u>I_2O_5:</u>

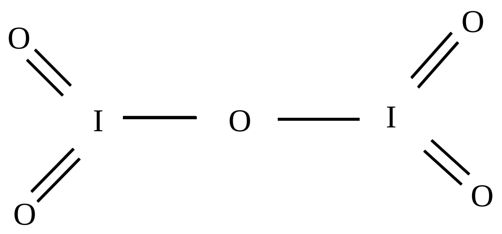
- White crystalline solid.
- It is an anhydride of HIO_3

$$2HIO_3 \xrightarrow[-H_2O]{170^0 C} I_2O_5$$

- It is useful analytical reagent for estimation of CO
- Hygroscopic

  ∴ commercial sample has formula $I_2O_5 . HIO_3$.

Structure:



Three dimensional with strong I ….O interaction (in solid state).

Oxy acids of Halogen:

- 'F' can't form stable oxy acids.

1. Hypo halous acids:

General formula : H O X

Structure : $\ddot{\underset{..}{X}} - OH$

eg. HOCl, HOBr & HOI

All are weak acids and are known only in solution. Strongly oxidising.

- Acidic character: HOCl > HOBr > HOI

  [The acidic character depends on electro negativity of central atom, higher the electro negativity greater the acidic character].

- Stability: HOCl > HOBr > HOI

  [Depends on strength of X – OH bond. X – OH strength decreases, stability decreases]

- Basic character of conjugate bases:

  $OCl^- < OBr^- < OI^-$

  [Weaker acid form strong conjugate base]

- All are prepared by shaking halogen water with HgO.

  $HgO + X_2 + H_2O \rightarrow HgX_2HgO + HOX$.

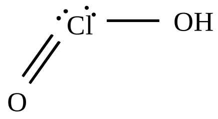
- In alkaline medium hypohalite ions disproportionate

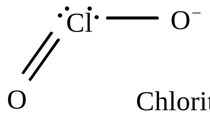
  $3XO^- \rightarrow 2X^- + XO_3^-$

- NaOCl sodium hypochlorite extensively used for bleaching cotton fabric and as a domestic bleach.

2. Halous acid: only $HClO_2$ known and exists in solution.

Preparation: $Ba(ClO_2)_2 + H_2SO_4 \rightarrow HClO_2 + BaSO_4$





Chlorite

☞ $NaClO_2$ sodium chlorite used as bleach and prepared from ClO_2 & NaOH or ClO_2 & Na_2O_2.

$$ClO_2 + NaOH \rightarrow \underset{(\text{Chlorite})}{NaClO_2} + NaClO_3 + H_2O$$

$$ClO_2 + Na_2O_2 \rightarrow NaClO_2 + O_2$$

3. <u>Halic acids:</u>

General formula HXO_3

Strong oxidising and strong acids

$$\text{Structure : } O = \overset{\overset{O}{\|}}{\underset{..}{X}} - OH$$

$$\underbrace{HClO_3 \qquad HBrO_3}_{\substack{\text{exist in solution} \\ (\text{not very stable})}} \qquad \underset{\text{stable(Solid)}}{HIO_3}$$

<u>Preparation:</u>

$Ba(XO_3)_2 + H_2SO_4 \rightarrow HXO_3 + BaSO_4$.

(X = Cl, B_r)

$$I_2 + \underset{\text{conc}}{HNO_3} \rightarrow HIO_3 + NO_2 + H_2O$$

Acidic character:

$$HClO_3 > HBrO_3 > HIO_3$$

(Based on electro negativity of halogens).

Stability : $HClO_3 < HBrO_3 < HIO_3$

<u>Uses of chlorates:</u> Sodium chlorate explodes on grinding

$NaClO_3$: used in fireworks, matches, weed killer.

$$KClO_3 \xrightarrow[400-500]{} KCl + O_2$$

$$KClO_3 \xrightarrow[150]{MnO_2} KCl + O_2$$

$$KClO_3 \xrightarrow[\substack{\text{catalyst} \\ \text{low temperature}}]{\text{absence of}} KClO_4 + Cl^-$$

4. **<u>Perhalic acids:</u>**

General formula (HXO_4): $HClO_4$ and HIO_4 are existing.

$HClO_4$ perchloric acid (powerful oxidising when anhydrous one of the strongest acid known)

$$\underset{(\text{solu})}{NaClO_3} + H_2O \xrightarrow[-H_2]{\text{electrolysis}} NaClO_4 + H_2SO_4 \rightarrow HClO_4 + NaHSO_4$$

(commercial $HClO_4$ (70%) is dihydrate $HClO_4.2H_2O$. it is only oxy acid which can be separated as anhydrous by heating with $H_2S_2O_7$].

$Mg(ClO_4)_2$ Magnesium perchlorate (hygroscopic) known as anhydrone used in dry batteries as electrolyte and as desiccant.

$$\left[\begin{array}{c} O \\ \| \\ O = Cl - OH \\ \| \\ O \end{array}\right].$$

All group I perchlorates are soluble except K^+, Rb^+, Cs^+.

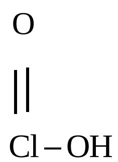
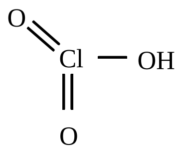
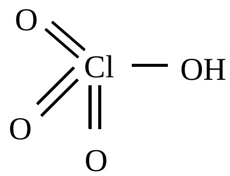
$\therefore$ K^+ quantitatively estimated as $KClO_4$.

Common form of periodic acid $HIO_4 . 2H_2O$ or H_5IO_6 known as para periodic acid.

Decomposes under vaccum on heating to form various periodic acids.

$$H_5IO_6 \xrightarrow[(2\text{moles}-3\text{moles}\,H_2O)]{80^0C} \underset{\text{dimeso periodic acid}}{H_4I_2O_9} \xrightarrow[(\text{one mole}-\text{one mole}\,H_2O)]{100^0C} \underset{\text{periodic acid}}{2HIO_4} \xrightarrow{200^0C} I_2O_5 + O_2 + H_2O$$

H_5IO_5 octahedral, weaker acid than $HClO_4$ but stronger oxidising than $HClO_4$.

Properties	Cl – OH	OCl OH	O_2ClOH	O_3ClOH
Structure	Cl – OH			
Acidic character	increases from left to right [higher the oxidation state greater the acidic character]			
Stability	increases from left to right [As the number of 'O' atoms increases number of bonds and stability increases]			
Stability of anion	$ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$ Due to resonance.			
Basic character of conjugate bases.	$ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$ Stronger acid can generate weaker conjugate base.			

Hydrides:

General formula : HX

General properties of hydrides:

Properties	HF	HCl	HBr	HI
Physical state	Liquid	gas	gas	gas
B.P	B.P $\propto$ Mol. Wt (only hydrides without 'H' bonding) HF > HI > HBr > HCl			
B.E & stability	HF > HCl > HBr > HI [bond length increases from HF to HI $\therefore$ bond energy & stability decreases].			
Reducing character	Reducing character $\propto \frac{1}{\text{B.E}}$ HF < HCl < HBr < HI			
Acidic character	Depends on bond energy of H – X bond (but not on electro negativity of halogen). HF < HCl < HBr < HI Bond energy decreases acidic character increases.			
Basic character of conjugate bases	$F^- > Cl^- > Br^- > I^-$ [strong acids form weak conjugate base].			
Composition of constant boiling mixture of acids.	36% $\left(\text{B.P } 120^0\right)$	20.4% $\left(110^0\right)$	47% $\left(126^0\right)$	57% $\left(127^0\right)$
Reaction with conc. H_2SO_4	No reaction	No reaction	Br_2	I_2

Hydrogen fluoride: Hydro fluoric acid is very corrosive

Industrial preparation:

$$CaF_2 + H_2SO_4 \rightarrow HF + CaSO_4$$

Note: CaF_2 should be free from SiO_2 other wise much of the HF is consumed.

$SiO_2 + HF \rightarrow SiF_4 + 2H_2O$

$SiF_4 + 2HF \rightarrow H_2[SiF_6]$.

- ☞ HF hydrogen bonded $(HF)_n$ zig . zag chain in both liquid and solid state.
- ☞ **Liquid HF as solvent:** (HF solvent has strong tendency to donate proton)
- ☞ Self ionisation.

$$2HF \rightleftharpoons [H_2F]^+ + F^-$$

☞ The substance which produces $[H_2F]^+$ in liquid HF is acid & the one which produces F^- is called base.

Eg: H_2SO_4, HNO_3 which are strong acids in aqueous solution behaves as bases in liquid HF

$HF + H_2SO_4 \rightarrow H_3\overset{+}{S}O_4 + F^-$

$HF + HNO_3 \rightarrow H_2\overset{+}{N}O_3 + F^-$

The strongest acid like $HClO_4$ behaves as amphoteric,

$$HF + \underset{(acid)}{HClO_4} \rightarrow H_2\overset{+}{F} + ClO_4^-$$

$$HF + \underset{(acid)}{HClO_4} \rightarrow HClO_4^+ + F^-$$

Preparation of HCl, HBr & HI:

$$NH_4Cl + \underset{conc}{H_2SO_4} \rightarrow HCl + (NH_4)_2SO_4$$

Similar method is not used for preparation of HBr, HI. Because concentrated H_2SO_4 oxidises HBr and HI to Br_2 & I_2 respectively.

$\therefore$ H_3PO_4 is used.

$Na X + H_2SO_4 \rightarrow HX + NaHSO_4$

(X = Br, I)

$$\underset{(Red)}{P} + X_2 \longrightarrow PX_3 \xrightarrow{H_2O} H_3PO_3 + HX$$

(X = Br, I)