OXYGEN FAMILY

1. OXYGEN (O₂)

Preparation

- (a) From oxides
- (i) By thermal decomposition of the oxides

$$3MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2$$

$$3Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$$

$$2\text{BaO}_2 \xrightarrow{\Delta} 2\text{BaO} + \text{O}_2$$

2HgO
$$\xrightarrow{450^{\circ}\text{C}}$$
 2Hg + O₂

$$2Ag_2O \xrightarrow{350^{\circ}C} 4Ag + O_2$$

(ii) By the action of water on sodium peroxide (Oxone)

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

(iii) By the action of conc. H_2SO_4 on MnO_2

$$2MnO_2 + 2H_2SO_4 \longrightarrow 2MnSO_4 + 2H_2O + O_2$$

- (b) From salts
- (i) Alkali metal nitrates on heating give out oxygen

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$

(ii) KClO₃, K₂Cr₂O₇ and KMnO₄ decompose at high temperatures evolving oxygen.

$$2\text{KClO}_3 \xrightarrow{400^{\circ}\text{C}} 2\text{KCl} + 3\text{O}_2$$

$$4 {\rm K_2Cr_2O_7} \xrightarrow{~400^{\circ}{\rm C}~} 4 {\rm K_2CrO_4} + ~2 {\rm Cr_2O_3} + ~3 {\rm O_2}$$

$$2\mathsf{KMnO_4} \xrightarrow{250\,^{\circ}\mathsf{C}} \mathsf{K_2MnO_4} + \ \mathsf{MnO_2} + \ \mathsf{O_2}$$

(iii) By heating KMnO₄ or K₂Cr₂O₇ with concentrated H₂SO₄.

$$4\mathsf{KMnO_4} + 6\mathsf{H_2SO_4} \longrightarrow 2\mathsf{K_2SO_4} + 4\mathsf{MnSO_4} + 6\mathsf{H_2O} + 5\mathsf{O_2}$$

$$2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

(iv) By adding H_2O_2 to acidified $KMnO_4$ solution.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

(c) Laboratory method

In laboratory, oxygen is prepared by heating of a mixture of potassium chlorate and manganese dioxide in 4:1 ratio. (MnO $_2$ used as a catalyst)

$$2KClO_{3} \xrightarrow{\quad MnO_{2} \\ \text{Potassiumchlorate} } 2KCl + 3O_{2}$$

(d) **Electrolysis of water**: Electrolysis of either acidified water using platinum electrodes or alkaline water using nickel electrodes is made in an electrolytic cell for obtaining oxygen and hydrogen.

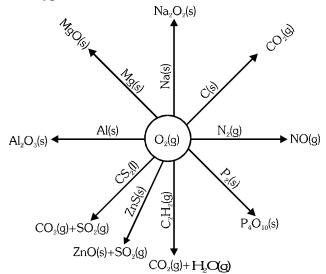
$$H_2SO_4 \Longrightarrow 2H^+ + SO_4^{2-}$$

At cathode :
$$2H^+ + 2e \longrightarrow H_2$$
 At anode : $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$

Properties

It is non inflammable but a supporter of combustion.

Some typical reactions of dioxygen -



2. OZONE (O₃)

Preparation

- (a) Unstable deep blue, diamagnetic gas, with fishy smell. Toxic enough (more toxic than KCN). It's intense blue colour is due to the absorption of red light.
- (b) Ozonised oxygen is separated by passing into spiral tube cooled by liquid air. Ozone condense at -112.4°C. [B.P. of O₂ -183°C; B.P. of liquid air is -190°C]

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$
$$F_2 + 3H_2O \longrightarrow 6HF + O_3$$

Properties

(a) Oxidising property

It is one of best oxidising agent, in acid solution, its standard, reduction potential value is 2.07V.

$$O_3 + 2H^+ + 2e \longrightarrow O_2 + H_2O$$
 $E^{\circ} = + 2.07 \text{ V}$

(i) Metal Sulphides to Sulphates.

$$MS + 4O_3 \longrightarrow MSO_4 + 4O_2$$
 [M = Pb, Cu, Zn, Cd]

(ii)
$$2HX + O_3 \longrightarrow X_2 + H_2O + O_2$$
 [X= Cl, Br, I]

(iii)
$$NaNO_2 + O_3 \longrightarrow NaNO_3 + O_2$$

 $Na_2SO_3 + O_3 \longrightarrow Na_2SO_4 + O_2$
 $Na_3AsO_3 + O_3 \longrightarrow Na_3AsO_4 + O_2$

(iv)
$$S + H_2O + 3O_3 \longrightarrow H_2SO_4 + 3O_2$$

 $2P + 3H_2O + 5O_3 \longrightarrow 2H_3PO_4 + 5O_2$
 $2As + 3H_2O + 5O_3 \longrightarrow 2H_3AsO_4 + 5O_2$

(v) Moist
$$I_2 \longrightarrow HIO_3 + 5O_2$$

$$I_2 + 5O_3 + H_2O \longrightarrow 2HIO_3 + 5O_2$$

$$Dry I_2 \longrightarrow I_4O_9 \text{ (yellow)}$$

$$2I_2 + 9O_3 \longrightarrow I_4O_9 + 9O_2$$

(vi)
$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

 $2K_4 [Fe(CN)_6] + O_3 + H_2O \longrightarrow 2K_3 [Fe(CN)_6] + 2KOH + O_2$
 $2FeSO_4 + O_3 + H_2SO_4 \longrightarrow Fe_2 (SO_4)_3 + O_2 + H_2O$

(vii) 2KI (acidified) +
$$O_3$$
 + 2HCl \longrightarrow I_2 + 2KCI + H_2O + O_2

$$2\text{KI}(\text{neutral}) + O_3 + 2\text{HCl} \longrightarrow \underbrace{I_2 + 2\text{KOH}}_{\text{KI+KOI}} + O_2 \\ \text{KI+KOI} + 2\text{HCl} \longrightarrow 2\text{KCl} + I_2 + H_2\text{O} \\ I_2 + 2S_2O_3^{2^-} \longrightarrow S_4O_6^{2^-} + 2\text{I} \\ \\ \text{alkaline} \begin{cases} \text{KI} + 3O_3 \longrightarrow \text{KIO}_3 + 3O_2 \\ \text{KI} + 4O_3 \longrightarrow \text{KIO}_4 + 4O_2 \end{cases}$$

(viii) Hg loses its fluidity (tailing of Hg)

$$2Hg + O_3 \longrightarrow Hg_2O + O_2$$
 Similarly
$$2Ag + O_3 \longrightarrow Ag_2O + O_2$$
Brown

(ix)
$$BaO_2 + O_3 \longrightarrow BaO + 2O_2$$

 $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
 $Na_2O_2 + O_3 + H_2O \longrightarrow 2NaOH + 2O_2$

(x)
$$2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$$

Note: In all above reaction O_3 gives up O_2 but some reactions are there which consumes all O-atom.

•
$$3SO_2 + O_3 \longrightarrow 3SO_3$$

$$\bullet \qquad 3 \\ SnCl_2 + 6 \\ HCl + \\ O_3 \\ \longrightarrow 3 \\ SnCl_4 + 3 \\ H_2O$$

Absorbent

- (a) Turpentine oil
- (b) Oil of cinnamon

Uses

- (a) Sterilizing water
- (b) Detection of position of the double bond in the unsaturated compound.

3. <u>HYDROGEN PEROXIDE</u> (H₂O₂)

Preparation

(a)
$$Na_2O_2 + H_2O \xrightarrow{\text{ice cold water}} 2NaOH + H_2O_2$$

(b)
$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

Instead of H_2SO_4 , H_3PO_4 is added now-a-days because H_2SO_4 catalyses the decomposition of H_2O_2 whereas H_3PO_4 favours to restore it.

$$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3H_2O_2$$

 $Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 + 2H_3PO_4$ (reused again)

(c) Electrolysis of $50\% \text{ H}_2\text{SO}_4$ using high current density.

$$2H_2SO_4 \Longrightarrow 2H^+ + 2HSO_4$$

At anode;
$$2HSO_4^- \longrightarrow H_2S_2O_8 + 2e$$
 At cathode; $2H^+ + 2e \longrightarrow H_2$ $H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$

$$(d) \qquad \bigodot C_2H_5 \xrightarrow{H_2/Pd} \bigodot OH \xrightarrow{O_2} C_2H_5 \xrightarrow{H_2/Pd} \bigodot OH$$

Properties

- (a) Colourless, odourless liquid (B.P.152°C)
- (b) Acidic nature

$$H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + H_2O$$

$$H_2O_2 + Ba(OH)_2 \longrightarrow BaO_2 + 2H_2O$$

$$H_2O_2 + Na_2O_3 \longrightarrow Na_2O_2 + H_2O + CO_2$$

(c) Oxidising and reducing nature

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O$$
 [acidic medium]
 $H_2O_2 + 2e \longrightarrow 2OH^-$ [alkali medium]

Oxidising nature

$$\begin{array}{l} \text{PbS} + 4\text{H}_2\text{O}_2 & \longrightarrow \text{PbSO}_4 + 4\text{H}_2\text{O} \text{ (Used in washing of oil painting)} \\ \text{NaNO}_2 + \text{H}_2\text{O}_2 & \longrightarrow \text{NaNO}_3 + \text{H}_2\text{O} \\ \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}_2 & \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \\ \text{Na}_3\text{AsO}_3 + \text{H}_2\text{O}_2 & \longrightarrow \text{Na}_3\text{AsO}_4 + \text{H}_2\text{O} \\ \text{2KI} + \text{H}_2\text{O}_2 & \longrightarrow \text{2KOH} + \text{I}_2 \\ \text{H}_2\text{S} + \text{H}_2\text{O}_2 & \longrightarrow \text{S}\downarrow + 2\text{H}_2\text{O} \end{array} \qquad \begin{array}{l} \text{X}_2 + \text{H}_2\text{O}_2 & \longrightarrow 2\text{HX} + \text{O}_2 & \text{X} = \text{Cl}, \text{Br}. \\ \text{Standered Reduction Potential order of } & \text{Cl}_2 > \text{Br}_2 > \text{H}_2\text{O}_2 > \text{I}_2 \end{array}$$

$$\begin{split} &H_2 S O_4 \, + \, 2 F e S O_4 \, + \, H_2 O_2 \, \longrightarrow \quad F e_2 (S O_4)_3 \, + \, 2 H_2 O \\ &2 K_4 \, [F e (C N)_6] \, + \, H_2 O_2 \, + \, H_2 S O_4 \, \longrightarrow \quad 2 K_3 [F e (C N)_6] \, + \, K_2 S O_4 \, + \, 2 H_2 O \\ &2 [C r (O H)_4]^- \, + \, 3 H_2 O_2 \, + \, 2 O H^- \, \longrightarrow \quad 2 C r O_4^{\, 2^-} \, + \, 8 \, \, H_2 O \\ &C r O_4^{\, 2^-} \, + \, 2 H^+ \, + \, 2 H_2 O_2 \, \longrightarrow \quad C r O_5 \, \, (B lue) \, \downarrow + \, 3 H_2 O \\ &4 C r O_5 \, + \, 1 2 H^+ \, \longrightarrow \quad 4 C r^{+3} \, + \, 7 O_2 \, + \, 6 H_2 O \\ &M n^{+2} \, + \, O H^- \, + \, H_2 O_2 \, \longrightarrow \quad M n O_2 \, + \, 2 H_2 O \, \, \text{(This reaction can be utilised to detect NH_3)} \end{split}$$

Reducing nature

$$\begin{array}{l} \operatorname{Ag_2O} + \operatorname{H_2O_2} \longrightarrow 2\operatorname{Ag} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{O_3} + \operatorname{H_2O_2} \longrightarrow \operatorname{H_2O} + 2\operatorname{O_2} \\ \operatorname{MnO_2} + \operatorname{H_2O_2} + \operatorname{H_2SO_4} \longrightarrow \operatorname{MnSO_4} + 2\operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{PbO_2} + \operatorname{H_2O_2} \longrightarrow \operatorname{PbO} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{PbO_3O_4} + \operatorname{4HNO_3} \longrightarrow \operatorname{2Pb}(\operatorname{NO_3})_2 + \operatorname{PbO_2} + 2\operatorname{H_2O} \\ \operatorname{PbO} + \operatorname{2HNO_3} \longrightarrow \operatorname{Pb}(\operatorname{NO_3})_2 + \operatorname{H_2O} \\ \operatorname{PbO} + 2\operatorname{HNO_3} \longrightarrow \operatorname{Pb}(\operatorname{NO_3})_2 + \operatorname{H_2O} \\ \operatorname{Pb_3O_4} + \operatorname{H_2O_2} + \operatorname{6HNO_3} \longrightarrow \operatorname{3Pb}(\operatorname{NO_3})_2 + \operatorname{4H_2O} + \operatorname{O_2} \\ \operatorname{X_2} + \operatorname{H_2O_2} \longrightarrow \operatorname{2HX} + \operatorname{O_2} [\operatorname{X} = \operatorname{Cl}, \operatorname{Br}] \\ \operatorname{2KMnO_4} + \operatorname{3H_2O_2} \longrightarrow \operatorname{2KOH} + \operatorname{2MnO_2} + \operatorname{2H_2O} + \operatorname{3O_2} \\ \operatorname{2MnO_4}^2 + \operatorname{2OH}^- \longrightarrow \operatorname{2MnO_2}^2 + \operatorname{4OH}^- + \operatorname{2O} \\ \operatorname{2MnO_4}^2 + \operatorname{2H_2O} \longrightarrow \operatorname{2MnO_2} + \operatorname{4OH}^- + \operatorname{2O} \\ \operatorname{2MnO_4}^2 + \operatorname{4H_2O} \longrightarrow \operatorname{2MnO_2} + \operatorname{4OH}^- + \operatorname{3O} \\ \operatorname{2KMnO_4} + \operatorname{5H_2O_2} + \operatorname{3H_2SO_4} \longrightarrow \operatorname{2MnSO_4} + \operatorname{K_2SO_4} + \operatorname{5O_2} + \operatorname{8H_2O} \\ \operatorname{2[Fe(CN)_6]^{3^-}} + \operatorname{2OH} - \operatorname{H_2O_2} \longrightarrow \operatorname{2[Fe(CN)_6]^{4^-}} + \operatorname{2H_2O} + \operatorname{O_2} \\ \operatorname{NaOCl} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaCl} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOCl} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaCl} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOCl} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaCl} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O_4} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O_4} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_3} + \operatorname{H_2O_4} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_2} \longrightarrow \operatorname{NaIO_4} + \operatorname{H_2O_4} + \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_4} \longrightarrow \operatorname{NaOO_4} + \operatorname{H_2O_4} + \operatorname{H_2O_4} - \operatorname{O_2} \\ \operatorname{NaOO_4} + \operatorname{H_2O_4} \longrightarrow \operatorname{NaOO_4} + \operatorname{H_2O_4} - \operatorname{O_4} \\ \operatorname{NaOO_4} + \operatorname{H_2O_4} \longrightarrow \operatorname{NaOO_4} + \operatorname{H_2O_4} - \operatorname{O_4} - \operatorname{H_2O_4} - \operatorname{H_2O$$

Uses

(a) As a rocket propellant

 $\mathrm{NH_2}$. $\mathrm{NH_2}$ + $\mathrm{2H_2O_2}$ \longrightarrow $\mathrm{N_2}$ + $\mathrm{4H_2O}$ [highly exothermic and large increase in volume]

(b) In detection of Cr^{+3} , Ti^{+4} etc.

4. <u>HYDROGEN SULPHIDE</u> (H₂S) <u>SULPHURATED HYDROGEN</u>

Preparation

By the action of dil. HCl or H₂ SO ₄on iron pyrites.

$$\text{FeS} + \text{H}_2 \text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2 \text{S} \uparrow$$

Note: The gas is then dried over fused $CaCl_2$ or P_2O_5 . Conc. H_2SO_4 cannot be used for drying purpose because H_9S oxidize to sulphur.

Properties

It is a colourless gas having an offensive smell of rotten eggs.

(a) It burn in air with blue flame

$$2H_{o}S + O_{o} \longrightarrow 2H_{o}O + S$$

If the air supply is in excess

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_3$$

(b) It is a mild acid.

$$H_9S \longrightarrow H^+ + SH^-$$

$$SH^- \longrightarrow H^+ + S^{-2}$$

(c) It act as a reducing agent. It reduces halogen into corresponding hydroacid.

$$H_2S + X_2 \longrightarrow 2HX + S$$

Tests of H₂S

- (a) Unpleasant odour resembling that of rotten eggs.
- (b) It turns lead acetate into paper black

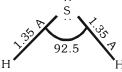
$$(CH_3 COO)_2 Pb + H_2 S \longrightarrow PbS \downarrow + 2 CH_3 COOH$$

Black

(c) It gives a violet colouration with a solution of sodium nitroprusside.

Structure of H_oS

(a) Similar to structure of water molecule i.e. V- shaped structure with bond length (H-S) 1.35A and bond angle (H-S-H) is 92.5 ...



Uses

- (a) It is mainly employed in salt analysis for the detection of cation.
- (b) Reducing agent for H_2SO_4 , $KMnO_4$, $K_2Cr_2O_7$, O_3 , H_2O_2 , $FeCl_3$

5. <u>SULPHUR DIOXIDE</u> (SO₂)

Preparation

Prepared by any of the following methods.

(a)
$$Cu + 2H_2 SO_4 \xrightarrow{\Delta, conc.} CuSO_4 + SO_2 + 2H_2 O$$

(b)
$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

(c) 4Fe
$$S_2 + 11O_2 \longrightarrow 2Fe_2 O_3 + 8SO_2$$

Properties

- (a) It has a pungent and suffocating odour.
- (b) It acts as lewis base due to presence of a lone pair of electrons.
- (c) Acidic nature

It dissolves in H₂O to give sulphurous acid, hence known as sulphurous anhydride.

$$SO_2 + H_2 O \longrightarrow H_2 SO_3$$

Due to acidic nature, it can react with bases to give salts.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

(d) Reducing nature

In the presence of moisture it can liberate nascent hydrogen or in presence of an oxidising agent it can easily take an oxygen atom.

$$SO_{2} \xrightarrow{\text{FeCl}_{3} + \text{H}_{2}O} H_{2}SO_{4} + \text{NO}_{2}$$

$$FeCl_{3} + \text{H}_{2}O + \text{H}_{2}SO_{4} + \text{HCl} + \text{FeCl}_{2}$$

$$KMnO_{4} + H_{2}SO_{4} + \text{M}_{1}SO_{4} + \text{H}_{2}SO_{4}$$

$$K_{2}SO_{4} + \text{M}_{1}SO_{4} + \text{H}_{2}SO_{4}$$

$$K_{2}SO_{4} + \text{Cr}_{2}(SO_{4})_{3} + \text{H}_{2}O$$

(e) Oxidising nature

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S \downarrow$$

 $SO_2 + 2CO \longrightarrow 2CO_2 + S \downarrow$

- (f) Bleaching nature
- (i) Sulphur dioxide acts as bleaching agent in the presence of water, it is oxidised with the liberation of nascent hydrogen which reduces the colouring matter to colourless.

$$SO_2+2H_2O \longrightarrow H_2SO_4+2$$
 [H]

Colouring matter + 2[H] — Colourless compound.

(ii) Since the colourless (reduced) compound is reoxidised by air to coloured compound, bleaching by ${\rm SO}_2$ is temporary.

Note: Chlorine has permanent bleaching action, so reaction is not reversible.

6. SULPHURIC ACID H₂ SO₄ (OIL OF VITRIOL)

King of chemical (due to very great commercial importance)

Preparation

 $H_2 SO_4$ is prepared by two methods

(a) Lead chamber process

The mixture containing SO₂, air & nitric oxide when treated with steam, sulphuric acid is formed.

Stage I : $2NO(Catalyst) + O_2 \longrightarrow 2NO_2$

Stage II : $2SO_2 + 2NO_2 \longrightarrow 2SO_3 + 2NO$

(b) Contact process

In this process SO₂ is oxidised by air in the presence of catalyst (platinised asbestos).

Stage I :
$$S + O_2 \xrightarrow{\Delta} SO_2$$

Stage II :
$$2SO_2 + O_2 \xrightarrow{v_2o_5} 2SO_3$$

Stage III :
$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$
 (oleum)

Stage IV : Sulphuric acid of any desired concentration can be obtained from oleum by

dilution with water

$$H_2 S_2 O_7 + H_2 O \longrightarrow 2H_2 SO_4$$

Chemical properties

- (a) As an oxidising agent
- (i) H_2SO_4 gives oxygen on strong heating, hot conc. H_2SO_4 acts as an oxidising agent.

$$H_2SO_4 \xrightarrow{\Delta} H_2O + SO_2 + [O]$$

(ii) Non metals oxidised to their oxides.

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

(iii) Dilute acid releases hydrogen with all metals except mercury, copper and noble metals.

$$H_2SO_4 + Zn \longrightarrow ZnSO_4 + H_2 \uparrow$$

Hot conc. H₂SO₄ releases SO₂ on reaction with metals.

$$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + 2H_2O + SO_2$$

(iv) Oxidation of compounds

$$2HX + H_2SO_4 \xrightarrow{\Delta} X_2 + SO_2 + 2H_2O$$
 (where X = Br or I)

- (b) As a dehydrating agent
- (i) Conc. $H_2 SO_4$ is a powerful dehydrating agent. Its corrosive action on skin is due to dehydration of skin which then burns and produces itching sensation.
- (ii) It's dehydrating property is due to strong affinity for water.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

This is called as charring of sugar.

$$CH_3 CH_2 OH \xrightarrow{\text{conc.H}_2SO_4} CH_2 = CH_2 + H_2 O$$

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

Uses

- (a) In the manufacture of fertilisers like ammonium sulphate, calcium superphosphate etc.
- (b) As a drying agent.

7. SODIUM THIOSULPHATE (Na,S,O, 5H,O)

Preparation

(a)
$$Na_2SO_3 + S$$
 (powder) $\xrightarrow{\text{boiling}} Na_2S_2O_3 \xrightarrow{\text{evaporation}} Na_2S_2O_3.5H_2O$, monoclinic crystal $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$ $2NaHSO_3 + Na_2CO_3 \longrightarrow 2Na_2SO_3 + H_2O + CO_2$ Excess

(b)
$$Na_2SO_4 + 4C \xrightarrow{roasting} 4CO + Na_2S \xrightarrow{SO_2} Na_2S_2O_3 + S$$

Salt cake Coke

(c)
$$2\text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + 4\text{SO}_2 \longrightarrow 3\text{Na}_2\text{S}_2\text{O}_3 + \text{CO}_2$$

(d)
$$6\text{NaOH} + 4\text{S} \longrightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S} + 3\text{H}_2\text{O}$$

 $3\text{Ca(OH)}_2 + 12\text{ S} \longrightarrow \text{CaS}_2\text{O}_3 + 2\text{CaS}_5 + 3\text{H}_2\text{O}$

(e)
$$Na_2SO_3 + Na_2S + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$$

(f)
$$2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$$

Properties

Action of $AgNO_3$: A white precipitate of silver thiosulphate is obtained by the action of $AgNO_3$ which changes to yellow, brown and finally black due to the formation of silver sulphide.

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NONO_3$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

Action of silver halides: Halides form complexes with sodium thiosulphate. Silver bromide forms argento thiosulphate complex.

This property is used in photography for fixing.

Action on copper sulphate: Cuprous thiosulphate is formed which dissolves in excess of sodium thiosulphate to form a complex.

Uses

- (a) As an antichlor to remove excess of chlorine from bleached fabrics.
- (b) In photography as a fixing agent in the name of hypo.
- (c) In the extraction of silver and gold.
- (d) As a reagent in iodometric and iodometric titrations for the estimation of iodine $CusO_4$, $K_2Cr_2O_7$, $KMnO_4$, Na_3AsO_3 etc.
- (e) Sodium hyposulphite $(Na_2S_2O_4)$ is used for reducing indigo or other vat dyes.

HALOGEN FAMILY

1. FLUORINE (F₂)

Preparation

Moissan's method

Electrolyte is a [KHF $_2$ (1 part) and anhydrous H_2F_2 (5 parts)]. 1 : 5 mixture of KHF $_2$ and anhydrous H_2F_2 . The reaction taking place in this method are :

Physical properties

- (a) Fluorine is a pale yellow gas which condenses to a clear yellow liquid having a density of 1.108 and B.P is $-187.7^{\circ}C$. At $-223^{\circ}C$ it freezes to a pale yellow solid and at $-252^{\circ}C$ the solid becomes colourless.
- (b) It is a pungent smelling and poisonous gas but less poisonous than HF gas.
- (c) It attacks organic matter and hence should be handled carefully.

Chemical Properties

(a) Reaction with water : Reaction is vigorous even in the dark giving O_2 and O_3

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

 $3F_2 + 3H_2O \longrightarrow 6HF + O_3$

(b) Reaction with hydrogen: F_2 combines with H_2 explosively even in the dark, forming HF.

$$F_2 + H_2 \longrightarrow 2HF$$

(c) Action on alkalies: Unlike Cl_2 , Br_2 and I_2 , F_2 reacts with dil. alkalies (2% solution) and forms NaF and OF_2 (not NaFO). With conc. alkalies F_2 gives NaF and O_2 (not NaFO₃).

$$2F_2$$
 + 2NaOH (2% solution) \longrightarrow 2NaF + OF₂ + H₂O
 $2F_2$ + 4NaOH (conc. solution) \longrightarrow 4NaF + O₂ + 2H₂O

(d) Oxidising property: Since F_2 has the largest positive value of standard reduction electrode potential for the reduction reaction.

$$F_{2(g)}$$
 + aq + e⁻ \longrightarrow $2F^{-}$

 F_2 is the strongest oxidising agent among all the halogens. Maximum oxidising power of F_2 is confirmed by the following reactions –

(i) Action of F_2 on halides: F_2 can liberate halogen from the aqueous solution of all the three halides (generally sodium or potassium halides) while other halogens connot do so.

$$F_2 + 2KX \longrightarrow 2KF + X_2 \quad (X = Cl, Br, I)$$

In the above reaction X^{-} is oxidised to X_{2} .

(ii) Action of F_2 on H_2O : F_2 oxidises (decomposes) H_2O to O_2 and O_3

$$2H_2O_{(I)} + 2F_{2(g)} \longrightarrow 4HF_{(aq)} + O_{2(g)}$$

 $3H_2O_{(I)} + 3F_{2(g)} \longrightarrow 6HF_{(aq)} + O_{3(g)}$

(e) Action on NH_3 : F_2 reacts with NH_3 to give N_2 and some NF_3

$$3F_2 + 2NH_3 \longrightarrow N_2 + 6HF$$

$$3F_2 + NH_3 \longrightarrow NF_3 + 3HF$$

(f) Action on H_2S : H_2S burns in an atmosphere of F_2 , forming SF_6 and HF

$$H_2S + 4F_2 \longrightarrow SF_6 + 2HF$$

 $Uses: F_2$ is used as an insecticide.

2. CHLORINE (Cl₂)

Preparation

(a) From HCl: HCl is most important chemical to prepare chlorine and HCl reacts with a number of oxidising agents to liberate Cl₂.

$$2HCl + [O] \longrightarrow Cl_2 + H_2O$$

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2 \uparrow$$

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2 \uparrow$$

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2 \uparrow$$

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2 \uparrow$$

$$O_3 + 2HCl \longrightarrow O_2 + H_2O + Cl_2 \uparrow$$

(b) From bleaching powder: Bleaching powder liberates Cl_2 when treated with mineral acid or CO_2 .

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

(c) From chlorides : Cl_2 may also be obtained by decomposing metal chlorides by MnO_2/H_2SO_4

$$2 \text{NaCl} + \text{MnO}_2 + 3 \text{H}_2 \text{SO}_4 - - - - - 2 \text{NaHSO}_4 + \text{MnSO}_4 + 2 \text{H}_2 \text{O} + \text{Cl}_2$$

- (d) Laboratory method: In laboratory, Cl_2 is prepared by action of HCl on MnO_2 or $KMnO_4$ or $K_2Cr_2O_7$
- (i) From MnO₂

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

(ii) From $K_2Cr_2O_7$ or $KMnO_4$

$$2\mathsf{KMnO}_4 + 16\mathsf{HCl} \longrightarrow 2\mathsf{KCl} + 2\mathsf{MnCl}_2 + 8\mathsf{H}_2\mathsf{O} + 5\mathsf{Cl}_2$$

$$K_2Cr_2O_7 + 14 HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

(iii) Preparation of pure Cl_2 : Cl_2 of high purity may be obtained by decomposing platinic chloride (PtCl₄) or gold chloride (AuCl₂)

$$PtCl_4 \xrightarrow{580^{\circ}C} Pt + 2Cl_2$$

$$2AuCl_3 \xrightarrow{300^{\circ}C} 2Au + 3Cl_2$$

Manufacturing (iv)

Weldon's process: This method involves the heating of pyrolusite (a mineral of Mn, contain MnO₂) with

$$MnO_2 + 4HCl \longrightarrow 2H_2O + MnCl_2 + Cl_2$$

MnCl₂ thus obtained is also used for production of Cl₂ by following process.

$$MnCl_2 + Ca(OH)_2 \longrightarrow Mn(OH)_2 + CaCl_2$$

$$2Mn(OH)_2 + O_2$$
 (air) $\longrightarrow 2MnO_2 + 2H_2O$

$$MnO_2 + Ca(OH)_2 \longrightarrow CaMnO_3 \downarrow + H_2O$$

Calcium mangnite

$$CaMnO_3 + 6HCl \longrightarrow CaCl_2 + MnCl_2 + Cl_2 \uparrow + 3H_2O$$

Deacon's process: In this method, HCl is oxidised by air in the presence of CuCl2 catalyst

$$4\text{HCl} + \text{O}_2 \xrightarrow{\text{CuCl}_2/450^{\circ}\text{C}} 2\text{H}_2\text{O} + 2\text{Cl}_2$$

The probable mechanism of the reaction is as

$$2CuCl_2 \longrightarrow Cl_2 + 2CuCl$$

$$4CuCl + O_2 \longrightarrow 2(CuO CuCl_2)$$

$$CuO CuCl_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$

Thus Cl₂ is formed continuously by oxidation of HCl.

By electrolysis of brine: Concentrated aqueous solution of NaCl is known as brine and on electrolysis of brine, Cl₂ is liberated at anode.

NaCl
$$\longrightarrow$$
 Na⁺ + Cl⁻ Ions present
H₂O \rightleftharpoons H' + OH in brine

at cathode
$$2H^+ + 2e^- \longrightarrow H_2$$
 (:: D.P._H⁺ < D.P._{Na}⁺)

$$(:: D.P.H^+ \le D.P.Na^+)$$

at anode
$$2Cl^{-} \longrightarrow Cl_{2}$$

Note: For electrolysis Nelson Cell or Solvay -Kellner cell are used.

By electrolysis of molten NaCl: Electrolysis of molten NaCl gives Cl2 at anode and Na metal at cathode. This method of extraction of Na is known as Down's process. Down's cell is composed of:

- Anode: Steel rod
- Cathode: Graphite
- Electrolyte: Mixture of molten NaCl, and NaF
- Temperature: 600°C

Following reactions take place in the cell

at cathode;
$$Na^+ + e^- \longrightarrow Na$$
 at anode; $2Cl^- \longrightarrow Cl_2 + 2e^-$

Nitrosyl chloride process: Common salt (NaCl) is treated with concentrated nitric acid, when a mixture of chlorine and nitrosyl chloride is evolved.

$$3NaCl + 4HNO_3 \longrightarrow 3NaNO_3 + NOCl_{(g)} + Cl_2 + 2H_2O$$

The gaseous mixture formed is also oxidised with oxygen.

$$2NOCl_{(g)} + O_2 \longrightarrow 2NO_2 + Cl_2$$

The gaseous mixture is liquefied which on distillation gives Cl₂

Physical Properties

- (a) It is yellow green, pungent smelling, toxic gas. It has toxic effect on lungs, throat and nose.
- (b) It gives chlorine water when passed through water which is strong oxidation. If passed through ice cold water, crystals of $\text{Cl}_2\ 8\text{H}_2\text{O}$ are obtained.
- (c) On liquifaction it gives yellow liquid (B.P. -34.6°C). Its f.p. is -101.1°C.
- (d) It is heavier (2.4 times) than air.

Chemical properties

(a) Reaction with Hydrogen : $H_2 + Cl_2 \xrightarrow{h_{N'}} 2HCl$

It reacts with ammonia under two conditions.

(i) When ammonia in excess

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

(ii) When chlorine in excess

$$\mathrm{NH_3}$$
 + $\mathrm{3Cl_2}$ \longrightarrow $\mathrm{NCl_3}$ + $\mathrm{3HCl}$

(b) Reaction with metals

$$2Na + Cl_2 \longrightarrow 2NaCl$$

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

$$Zn + Cl_2 \longrightarrow ZnCl_2$$

$$Cu + Cl_2 \longrightarrow CuCl_2$$

$$Mg + Cl_2 \longrightarrow MgCl_2$$

(c) Reaction with non metals

$$2S + Cl_2 \longrightarrow S_2Cl_2$$

$$2B + 3Cl_2 \longrightarrow 2BCl_2$$

(d) Oxidising and bleaching nature

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$

$$Cl_2 + H_2O \longrightarrow 2HCl + O$$

Coloured matter + (O) \longrightarrow Colourless matter

The bleaching action is permanent.

(i) Ferrous chloride or ferrous sulphate containing dilute H_2SO_4 , is oxidised to ferric chloride or ferric sulphate respectively.

$$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$$

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

(ii) Sulphites are oxidised to sulphates.

$$Na_2SO_3 + H_2O + Cl_2 \longrightarrow NaSO_4 + 2HCl$$

(iii) Moist sulphur dioxide is oxidised to H_2SO_4

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

(iv) Sulphur is precipitated from sodium thiosulphate.

$$Na_2S_2O_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + 2HCl + S$$

(v) Cl_2 oxidises I_2 to HIO_3 .

$$5Cl_2 + I_2 + 6H_2O \longrightarrow 10HCl + 2HIO_3$$

(e) Action of alkalies: When passed into cold dilute solution of alkalies, it forms chloride and hypochlorites.

2 NaOH +
$$Cl_2$$
 \longrightarrow NaCl + NaClO + H_2O

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + Ca(ClO)_2 + 2H_2O$$

However with hot concentrated alkali solutions it forms chlorates.

$$6$$
NaOH + 3 Cl₂ \longrightarrow 5 NaCl + NaClO₃ + 3 H₂O

$$6Ca(OH)_2 + 6Cl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$$

(f) Addition reactions: Chlorine forms addition compounds with SO_2 , CO and unsaturated hydrocarbons.

$$\mathsf{SO}_2 + \mathsf{Cl}_2 {\longrightarrow} \mathsf{SO}_2 \mathsf{Cl}_2$$

Sulphuryl chloride

$$CO + Cl_2 \longrightarrow COCl_2$$

Carbonyl chloride (phosgene)

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

Ethylene chloride

3. OXIDES OF CHLORINE

Dichloro oxide (Cl₂O)

Preparation: Cl2 does not combine directly to produce its oxides but indirect method are there.

Condensed to orange liquid

Properties

(a) It dissolves in water

$$Cl_{9}O + H_{9}O \longrightarrow 2HClO$$

(b) Explodes violently with NH₃

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

(c) It is oxidising agent

$$Cl_2O + 2HCl \longrightarrow 2Cl_2 + H_2O$$

(d) Structures.



Chlorine dioxide (ClO₂)

Preparation

- (a) $3KClO_3 + 3H_2SO_4 \longrightarrow 3KHSO_4 + HClO_4 + 2ClO_2 \uparrow + H_2O$ (powder) conc. pale yellow gas
- (b) $2HClO_3 + H_2C_2O_4 \xrightarrow{60^{9}C} 2H_2O + 2ClO_2 + 2CO_2$
- (c) $2 \text{AgClO}_3 + \text{Cl}_2 \xrightarrow{90^{\circ}\text{C}} 2 \text{AgCl} + 2 \text{ClO}_2 + \text{O}_2$ [By this reaction pure ClO_2 obtained]

Properties

(a) ClO₂ dissolves in water producting dark green solution which decomposes in presence of light.

$${\rm ClO_2} {\:\longrightarrow\:} {\:\rm ClO} \, + \, {\rm O}$$

2ClO +
$$H_2O$$
 \longrightarrow HCl + $HClO_3$

(b) But in alkali gives a mixture of chlorite and chlorate. It is a powerful oxidising and bleaching agent.

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

$$2ClO_2 + 2NaOH + H_2O_2 \longrightarrow 2NaClO_2 + O_2 + 2H_2O$$

(c) ${
m ClO}_2$ does not dimerise because odd electron undergoes delocalisation (in its own vaccant 3d-orbital)

 ${\rm Cl_2O_4}$ (Cl.ClO_4) is not the dimer of ${\rm ClO_2}.$ Actually it is Cl-perchlorate.

$$CsClO_4 + ClOSO_2F \longrightarrow Cs(SO_3)F + ClOClO_3$$

Dichlorine Hexoxide (Cl₂O₆)

Preparation

$$2ClO_2 + 2O_3 \xrightarrow{O^{\circ}C} Cl_2O_6 + 2O_2$$

$$\mathrm{Cl_2O_6}$$
 \longrightarrow $2\mathrm{ClO_3}$ (monomer is paramagnetic)

Properties

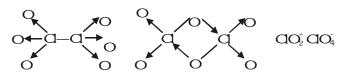
$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

$$Cl_2O_6$$
 + NaOH \longrightarrow NaClO $_3$ + NaClO $_4$ + H $_2$ O

$$Cl_2O_6 + HF \longrightarrow ClO_2F + HClO_4$$

$$Cl_2O_6 + NO_2 \longrightarrow ClO_2 + [NO_2]^+ [ClO_4]^-$$

Structures



 $liq \longrightarrow dark red$

Solid
$$\longrightarrow$$
 Yellow

Clorine Heptoxide (Cl₂O₇)

It is the anhydride of HClO₄ and perpared from it by the reaction of P₂O₅

Preparation

$$2HClO_4 + P_2O_5 \longrightarrow 2HPO_3 + Cl_2O_7$$

Properties: It is colourless liquid which is explosive in nature.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$
 (perchloric acid)

Structure

4. BROMINE (Br₂)

(a) From Brine water: Contains 65 ppm of Br-

$$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$$
 (Br $_2$ is volatile in nature)

Hence it is collected by

(i) Removal of Br₂ vapour by steam of air.

(ii) Absorbing it into Na₂CO₃ Solution

$$Br_2 + 6OH^- \longrightarrow Br^- + BrO_3^- + 3H_2O$$

Then acidified to get pure Br₂

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

5. \underline{IODINE} (I₂)

Chille salt petre contains traces of $NaIO_3$ which is reduced to \bar{I} by $NaHSO_3$, then oxidation of \bar{I} to \bar{I}_2 by $\bar{IO_3}$.

$$2IO_3^- + 6 HSO_3^- \longrightarrow 2I^- + 6SO_4^{2-} + 6H^+$$

 $5I^- + IO_3^- \xrightarrow{6H^+} 3I_2 + 3H_2O$

6. HALOGEN ACIDS

Preparation

All the halogens combine directly with hydrogen to form halogen acids but their reactivity decreases progressively from fluorine to iodine.

$$H_2 + X_2 \longrightarrow 2HX (X=F, Cl,Br \text{ or } I)$$
 $H_2(g) + Br_2(g) \xrightarrow{Pt/asbestos} 2 HBr$

A mixture of calcium fluoride (fluorite of fluorospar) and sodium chloride with concentrated sulphuric acid.

$$\begin{aligned} &\operatorname{CaF_2(s)} + \operatorname{H_2SO_4(aq)} & \longrightarrow \operatorname{CaSO_4(s)} + \operatorname{2HF(g)} \\ &\operatorname{2NaCl(s)} + \operatorname{H_2SO_4(aq)} & \longrightarrow \operatorname{Na_2SO_4(s)} + \operatorname{2HCl(g)} \end{aligned}$$

 H_2SO_4 is not satisfactory for the preparation of HBr and HI because the HBr or HI formed are oxidised by H_2SO_4 and the product is contaminated with the respective halogen. This difficulty can be overcome by using a non-oxidizing acid such as H_3PO_4 .

$$2\text{NaI} + \text{H}_2 \text{SO}_4 \longrightarrow \text{Na}_2 \text{SO}_4 + 2\text{HI}$$

$$2\text{HI} + \text{H}_2 \text{SO}_4 \longrightarrow 2\text{H}_2 \text{O} + \text{SO}_2 + \text{I}_2$$

Physical properties

- (a) Except HF (due to presence of H-bond) all hydrogen halides are gases
- (b) These can be liquified.
- (c) Covalent character: The bonds between H & X have some degree of polarity in the following order.

 HF > HCl > HBr > HI
- (d) Thermal stability: Thermal stability of the hydrides decreases from HF to HI i.e. HF >HCl >HBr > HI. This is due to the reason that as the size of the halogen increases from F to I the bond dissociation energy decreases.
- (e) Boiling point or volatility
- (i) Because of high electronegativity, H-F forms strong H-bonds.
- (ii) As a result, it exists as an associated molecule, (HF)_n and hence is a liquid at room temperature while all other halogen acids are gases.
- (iii) However, after a sudden drop in boiling point from HF to HCl, the boiling points of other hydrides gradually increases from HCl to HI because of increase in size of the halogen from Cl to I.
- (iv) In other words volatility decreases in the order. HCl >HBr>Hl>HF.

Chemical properties

- (a) Acidic Strength
- (i) In gaseous state these are covalent but in aqueous solutions they ionise and act as acids.
- (ii) The relative strength increases from HF to HI according to their dissociation constant K.
- (iii) The acidic strength of halogen decreases from HI > HBr > HCl > HF.
- (iv) This is due to the reason that as the size of halogen increases, H-X bond becomes weaker and hence breaks easily to split off a proton.
- (b) Reducing property
- (i) The reducing nature increases from HF to HI as the stability decreases from HF to HI.
- (ii) HF does not show reducing nature. It can not be oxidised even by strong oxidizing agents.
- (c) Action of ammonia

$$NH_3 + HX \longrightarrow NH_4 X$$
 (Where X = Cl,Br,l) White fumes

(d) Action of halogens

Chlorine is liberated from HCl only by fluorine Br_2 is liberated from HBr by Cl_2 and F_2 only (not by l_2).

$$2HCl + F_2 \longrightarrow HF+Cl_2$$
 $2Hl + Br_2 \longrightarrow 2HBr + l_2$

Abnormal Properties of HF

- (a) Liquid at room temperature due to H bonding.
- (b) Most thermal stable then other halogen hydrides.
- (c) It is weak acid but is extremely stable. It is not oxidised by strong oxidising agents. On the other hand all other halogen acid is oxidised.
- (d) HF form two type of salt $(NaHF_2, Na_2F_2)$
- (e) This acid attacks on silica of glass & formation of following compounds.

$$SiO_2 + 2H_2F_2 \longrightarrow SiF_4 + 2H_2O$$
 $Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$
 $CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$
 $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$
 $SiF_4 + 2HF \longrightarrow H_2SiF_6$

7. OXY ACID OF HALOGEN FAMILY

Name of the acids and	Oxidation state		Oxoacids		Structure	Stability	Acidic strength
their salts	in the acid	а	Br	I			ou digii.
Hypohalous Hypohalite	+1	HOO	HBrO	HIO	H-O-X	Decreases	Increases
Halous, Halites	+3	HClO ₂			H-O-X->O	Decreases	Increases
Halic, Halates	+5	HClO₃	HB _r O₃	HO₃	O ↑ H-O-X→O	Decreases	Increases
Perhalic, Perhalates	+7	HClO ₄	HBrO ₄	HIO ₄	O ↑ HO-X→O ↓ O	Decreases	Increases

Oxidising power : $HOX > HXO_2 > HXO_3 > HXO_4$

Thermal stability: $HOX \le HXO_2 \le HXO_3 \le HXO_4$

(a) Fluoric (I) acid (HOF) : it is obtained when $\rm F_2$ is passed over ice at 273 K.

$$F_2 + H_2O$$
 = HOF + HF

It is colourless unstable gas which decomposes to HF and O_2 . It is strong oxidising agent and oxidises H_2O to H_2O_2 .

(b) Hypochlorous acid or chloric (I) acid (HOCl): It can be prepared by following reactions.

$$\begin{split} & 2 \text{HgO} \, + \, 2 \text{Cl}_2 \, + \, \text{H}_2 \text{O} \longrightarrow & \text{Hg}_2 \text{OCl}_2 \, + \, 2 \text{HOCl} \\ & 2 \text{CaOCl}_2 \, + \, \text{H}_2 \text{O} \, + \, \text{CO}_2 \longrightarrow & \text{CaCl}_2 \, + \, \text{CaCO}_3 \, + \, 2 \text{HOCl} \end{split}$$

It is stable only in solution whose dilute solution is colourless while concentrated solution is yellow. It decomposes as

2HOCl
$$\longrightarrow$$
 2HCl + O₂

weak acid and with Mg it evolves H_2

$$Mg + 2HCIO \longrightarrow Mg(CIO)_2 + H_2$$

It is powerful bleaching and oxidising agent due to evolution of nascent oxygen.

$$HOCl \longrightarrow HCl + [O]$$

(c) Chlorous acid or chloric (III) acid (HClO₂): It is also known in aqueous solution and can be prepared by following reactions.

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_2$$

It fresh solution is colourless but soon it turns yellow due to formation of ClO2

It shows disproportionation reaction as

It liberates I₂ from KI.

$$4KI + HClO_2 + 2H_2O \longrightarrow 4KOH + HCl + 2I_2$$

Its shape is angular with sp³ hybridised Cl-atom.

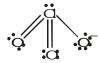


(d) Chloric acid ($HClO_3$): It is stable in aquous solution only. It is prepared by action of conc. H_2SO_4 on barium chlorate.

$$6Ba(OH)_2 + 6Cl_2 \longrightarrow Ba(ClO_2)_2 + 5BaCl_2 + 6H_2O$$

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_3$$

It is colourless pungent smelling liquid. It is stable in dark but decomposes in light. It acts as both oxidising and bleaching agent. Chlorate ion is pyramidal in geometry and central Cl-atom is sp³ hybridised.



(e) Perchloric acid (HClO₄): It most stable among oxoacids of chlorine. It is prepared by following reaction.

In anhydrous form, it can be prepared by distillation of mixture of $KClO_4$ and 96-97% of H_2SO_4 .

$$KClO_4 + H_2SO_4 \xrightarrow{90-160^{\circ}C} HClO_4 + KHSO_4$$

Anhydrous $HClO_4$ is colourless oily liquid which turns dark on standing. If fumes is moist air.

It is amongst strongest protonic acids known.

$$HClO_4 \longrightarrow H^+ + ClO_4^-$$

It is strong oxidising agent and explodes when comes in contact of organic matter. It dissolves most of the metals.

In ClO_4^- , central Cl-atom is sp^3 hybridised and so its structure is tetrahedral.

8. INTER HALOGEN

Types	AX	AX ₃	AX_5	AX ₇
	ClF	ClF ₃	ClF ₅	IF ₇
	BrF	BrF_3	BrF_5	
	BrCl	$(ICl_3)_2$	IF_5	
	ICI	IF ₃ (unstable)		
	IBr			
	IF (unstable)			

Properties

(i)
$$BrF_5 + 3H_2O \longrightarrow HBrO_3 + 5HF$$

(ii)
$$IF_5 + 3H_2O \longrightarrow HIO_3 + 5HF$$

(iii) IF₇ + H₂O
$$\longrightarrow$$
 IOF₅ + 2HF less
4H₂O \longrightarrow HIO₄ + 7HF $\}$ Parallel reaction

(iv) CIF is highly reactive and as a fluorinating agent.

$$\begin{aligned} & \text{6CIF} + 2\text{Al} & \longrightarrow 2\text{AlF}_3 + 3\text{Cl}_2 \\ & \text{6CIF} + \text{U} & \longrightarrow \text{UF}_6 + 3\text{Cl}_2 \\ & \text{6CIF} + \text{S} & \longrightarrow \text{SF}_6 + 3\text{Cl}_2 \\ & \text{CIF} + \text{SF}_4 & \longrightarrow \text{SF}_5 \text{Cl} \end{aligned}$$

One pecularity with ICl

In II^{nd} case, the attacking species is I^+ which has been supported by the formation of I^+ in fused state as follows: $3ICI \longrightarrow [I_2CI]^+ + [ICI_2]^-$

ICl₃ does not exist but its dimer exist.

$$2ICl_3 = I_2Cl_6$$

Structure:

(v) I_2Cl_6 : liquid has appreciable electrical conductivity like other interhalogens.

Characteristics

- $\bullet~$ 5IF $\longrightarrow~$ IF $_{\rm 5}$ + 2I $_{\rm 2}$ [The overall system gains B.E. by 250 kJ/mol]
- There are never more than two halogens in a molecule.
- Bonds are essentially covalent and B.P. increases as the E.N. difference increases.
- AX5 & AX7 type formed by large atoms like Br & I to accommodate more atoms around it.
- \bullet The interhalogens are generally more reactive than the halogens (except F_2) due to weaker A-X bonds compared to X-X bonds.

$$ICl + H_2O \longrightarrow HCl + HOI$$

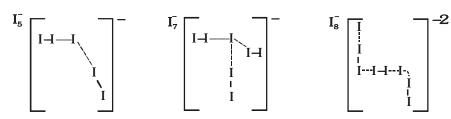
9. POLYHALIDES

Preparation and properties

- (a) $KI + I_2 \longrightarrow KI_3$
- (b) $ICl + KCl \longrightarrow K^{\dagger}[ICl_{o}]^{\dagger}$
- (c) $ICl_3 + KCl \longrightarrow K^{\dagger}[ICl_A]^{\dagger}$
- (d) $IF_5 + CsF \longrightarrow Cs^{\dagger}[IF_6]^{-}$
- (e) $ICl + KBr \longrightarrow K^{+}[BrICl]^{-}$
- (f) $Rb[ICl_2] \xrightarrow{\Delta} RbCl + ICl$ [not RbI + Cl₂]

Note: Here the products on heating depends on the lattice energy of the product halide. The lattice energy of alkali halide with smaller halogen is highest since the interatomic distance is least.

Structure



Ex. $[N(CH_3)_4]^+I_7^-, Cs_2I_8$

- \bullet Only F_3^- not known [due to absence of d-orbital] [i.e. $\mathrm{Cs}_2~\mathrm{I}_3$ I_2 $\mathrm{I}_3\mathrm{J}$
- I_3^- , Br_3^- , Cl_3^- are known Cl_3^- compounds are very less.
- Stability order : $I_3^- > Br_3^- > Cl_3^-$: depends upon the donating ability of X^- .

10. PSEUDO HALOGEN

There are univalent ion consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. **Ex.**

- (a) Na-salts are soluble in water but Ag-salts are insolubler in water.
- (b) H-compounds are acids like HX.
- (c) Some anions can be oxidised to give molecules \boldsymbol{X}_2 .

Anions	Acids	Dimer		
CN-	HCN	$(CN)_2$		
SCN-	HSCN (thiocyanic acid)	(SCN) ₂		
SeCN-		$(SeCN)_2$		
OCN-	HOCN (cyanic acid)			
NCN ²⁻ (Bivalent)	H ₂ NCN (cyanamide)			
ONC-	HONC (Fulminic acid)			
N - 3	HN_3 (Hydrazoic acid)			
CN^Θ shows maximum similarites with Cl-, Br-, I-				

- (d) forms HCN
- (e) forms $(CN)_2$
- (f) AgCN, Pb(CN)₂, are insoluble
- (g) Interpseudo halogen compounds CICN, BrCN, ICN can be formed.
- (h) AgCN is insoluble in H_2O but soluble in NH_3
- (i) forms large number of complex Ex. $[Cu(CN)_4]^{3-}$ & $[CuCl_4]^{-3}$

 $[Co(CN)_6]^{-3} \& [CoCl_6]^{-3}$

NOBEL GASES

1. INTRODUCTION

(a) The relative abundance in dry air by volume (ppm) of different noble gases is :

 He
 Ne
 Ar
 Kr
 Xe
 Rn

 5.24
 18.18
 93.40
 1.14
 0.09
 traces

(b) The melting points (K) for different noble gases are given as under:

He Ne Ar Kr Xe Rn
- 24.6 83.3 115.9 161.3 202.0

(c) The boling point (K) for different noble gases are given as under:

 He
 Ne
 Ar
 Kr
 Xe
 Rn

 4.2
 27.1
 87.3
 119.7
 165.0
 211

(d) The atomic radii (pm) for different noble gases are :

 He
 Ne
 Ar
 Kr
 Xe
 Rn

 93
 112
 154
 167
 190

(e) The vander wall's radii (pm) of differnet noble gases are given below:

 He
 Ne
 Ar
 Kr
 Xe
 Rn

 120
 160
 191
 200
 220

(f) The ionization energy values (kJ mol⁻¹) for different noble gases are given below:

 He
 Ne
 Ar
 Kr
 Xe
 Rn

 2372
 2080
 1520
 1351
 1170
 1037

(g) The enthalpies of vaporization, ΔH vapoure (kJ mol⁻¹) for noble gases are given below:

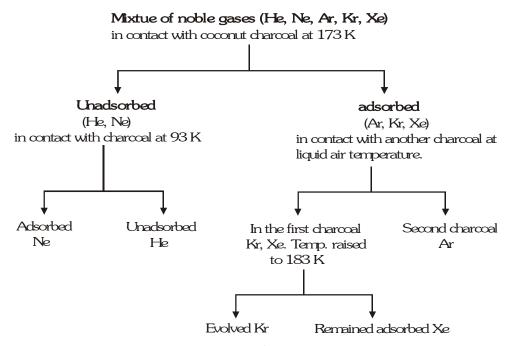
 He
 Ne
 Ar
 Kr
 Xe
 Rn

 0.08
 1.74
 6.52
 9.05
 12.65
 8.1

- (h) $\frac{Cp}{Cv}$ for noble gases is 1.67.
- (i) The refractive index, dielectric constant and other physical properties of noble gases correspond to their monoatomic nature.
- (j) The most important source of noble gases is atmosphere in which they are present in following proportions by volume and mass:

Element	Percentage by volume	Percentage by mass
Не	0.0006	0.000037
Ne	0.0015	0.001
Ar	0.932	1.285
Kr	0.0001	0.00028
Xe	0.00001	0.00004

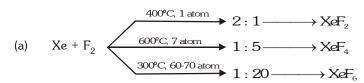
- (k) Helium is present to the extent of 2% in natural gas found in the united states and Canada.
- (l) Helium is also present in the minerals of radioactive elements uranium and thorium **Ex.** clevite, uranite, thorianite, monazite, pichblende etc.
- (m) The sixth member of the zero group was discovered in 1900 by Dorn as one of the disintegration products of radium and was named radon or nitron.
- (n) In Dewar's method, the separation of noble gases are summerized below:



- (o) The viscosity of He is extermely low, about $\frac{1}{100}$ th of hydrogen gas.
- (p) The thermal conductivity of He is very high about 800 times that of copper at room temperature
- (q) The lifting power of He is 92% that of hydrogen.
- (r) Helium is used for filing airships and balloons for meteorological abservations.
- (s) Mixture of He with O_2 under pressure is supplied to sea divers for respiration.
- (t) Helium is used to provide inert atmosphere in the welding of metals or alloys that are easily oxidized.
- (u) Helium (density 2) is lighter than that of air (density 14.4) and is used for inflating the tyres of big aeroplanes.
- (v) Neon is used to produce glow sign boards.
- (w) Argon mixed with $26\%~N_2$ is used in gas filled electric lamps and in radio valves and tubes.
- (x) Krypton and xenon have not been prepared in large quantities and have not been employed for a useful purpose.
- (y) Radon is used in radioactive research and in radiotherapy for the treatment of cancer.

2. Xe-COMPOUNDS

Xenon fluorides



- (b) H_2 reduces Xe-fluorides to Xe $XeF_2 + H_2 \longrightarrow Xe + 2HF$
- (c) Xe-fluorides oxidise Cl^- to Cl_2 and l^- to l_2 $XeF_2 + 2HCl \longrightarrow 2HF + Xe + Cl_2$ $XeF_4 + 4Kl \longrightarrow 4KF + Xe + 2I_2$
- (d) Hydrolysis

XeF2 reacts slowly with water

$$XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

 ${
m XeF_4}$ and ${
m XeF_6}$ react violently with water giving ${
m XeO_3}$

$$3 \text{XeF}_4 + 6 \text{H}_2 \text{O} \longrightarrow 2 \text{Xe} + \text{XeO}_3 + 12 \text{HF} + \frac{3}{2} \text{O}_2$$

$$\text{XeF}_6 + 3 \text{H}_2 \text{O} \longrightarrow \text{XeO}_3 + 6 \text{HF}$$

(explosive, white hygroscopic solid)

- (f) Xe-fluorides are also hydrolysed in alkaline medium $2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2$ $XeF_6 + 7OH^- \longrightarrow HXeO_4^- + 3H_2O + 6F^-$ Xenate ion

$$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} \downarrow + Xe + 2H_2O + O_2$$

- (g) They are used as fluorinating agent $2SF_4 + XeF_4 \longrightarrow 2SF_6 + Xe$
 - $Pt + XeF_4 \longrightarrow PtF_4 + Xe$
- (h) Act as a fluoride donor $XeF_2 + MF_5 \longrightarrow [XeF]^+ [MF_6]^- \qquad (M = As, Sb, P)$ $XeF_6 + BF_3 \longrightarrow [XeF_5]^+ [BF_4^-]$

 $XeF_c + HF \longrightarrow [XeF_s]^+ [HF_o]^-$