

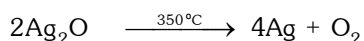
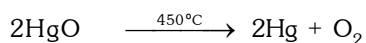
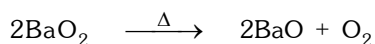
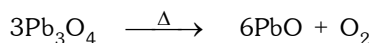
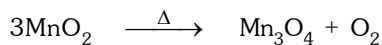
# OXYGEN FAMILY

## 1. OXYGEN (O<sub>2</sub>)

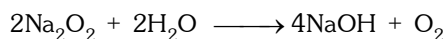
### Preparation

#### (a) From oxides

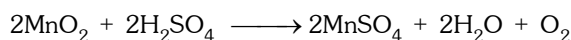
(i) By thermal decomposition of the oxides



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

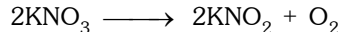
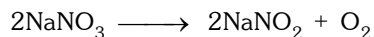


(iii) By the action of conc. H<sub>2</sub>SO<sub>4</sub> on MnO<sub>2</sub>

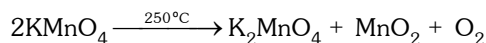
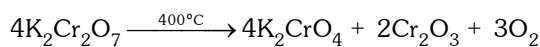
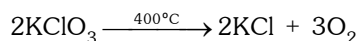


#### (b) From salts

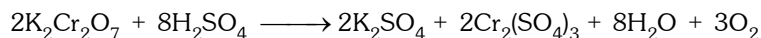
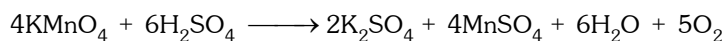
(i) Alkali metal nitrates on heating give out oxygen



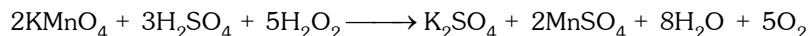
(ii) KClO<sub>3</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and KMnO<sub>4</sub> decompose at high temperatures evolving oxygen.



(iii) By heating KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with concentrated H<sub>2</sub>SO<sub>4</sub>.

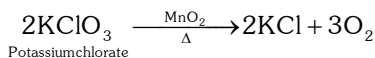


(iv) By adding H<sub>2</sub>O<sub>2</sub> to acidified KMnO<sub>4</sub> solution.

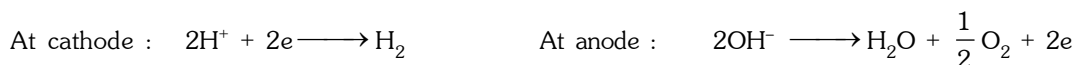
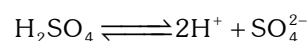


#### (c) Laboratory method

In laboratory, oxygen is prepared by heating of a mixture of potassium chlorate and manganese dioxide in 4 : 1 ratio. (MnO<sub>2</sub> used as a catalyst)



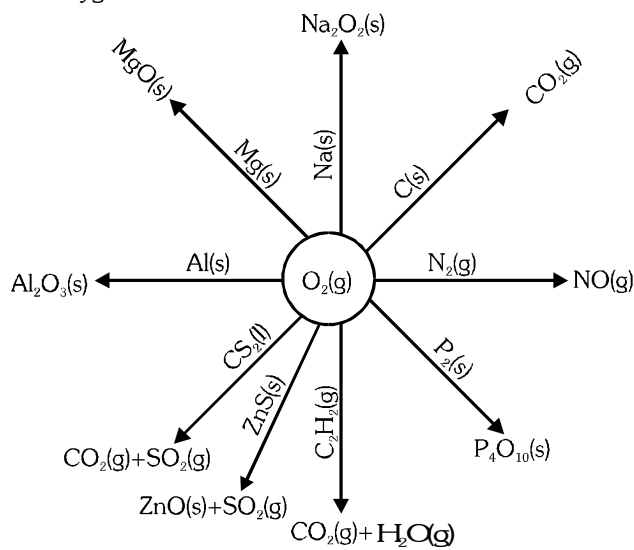
(d) **Electrolysis of water** : Electrolysis of either acidified water using platinum electrodes or alkaline water using nickel electrodes is made in an electrolytic cell for obtaining oxygen and hydrogen.



## Properties

It is non inflammable but a supporter of combustion.

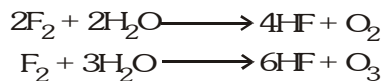
Some typical reactions of dioxygen –



## 2. OZONE ( $O_3$ )

### Preparation

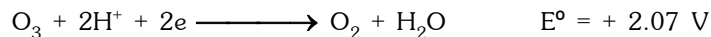
- (a) Unstable deep blue, diamagnetic gas, with fishy smell. Toxic enough (more toxic than KCN). Its intense blue colour is due to the absorption of red light.
- (b) Ozonised oxygen is separated by passing into spiral tube cooled by liquid air. Ozone condense at  $-112.4^\circ C$ . [B.P. of  $O_2$  –  $183^\circ C$  ; B.P. of liquid air is  $-190^\circ C$ ]



### Properties

#### (a) Oxidising property

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

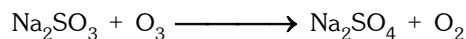


#### (i) Metal Sulphides to Sulphates.

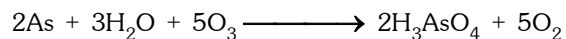
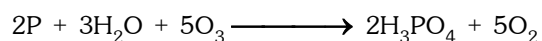


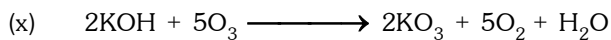
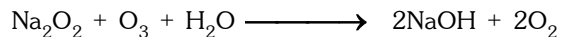
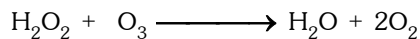
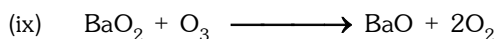
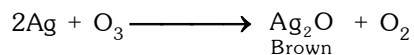
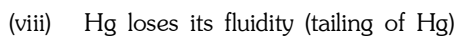
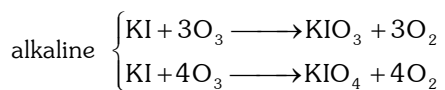
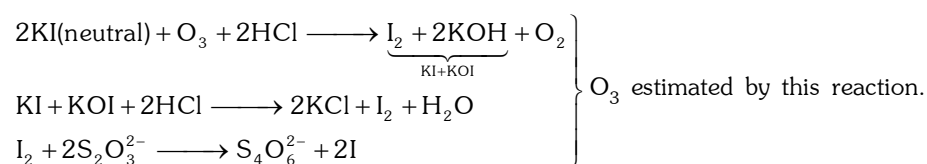
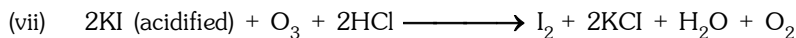
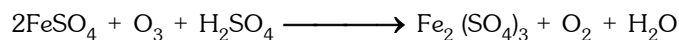
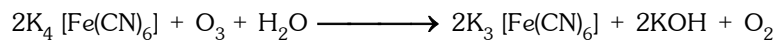
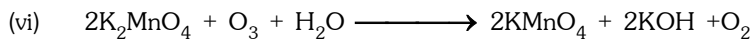
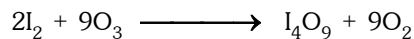
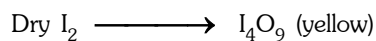
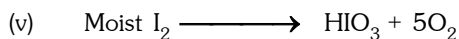
#### (ii) $2HX + O_3 \longrightarrow X_2 + H_2O + O_2$ [X= Cl, Br, I]

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

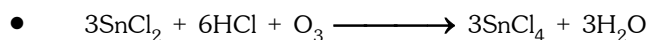
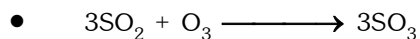


#### (iv) $S + H_2O + 3O_3 \longrightarrow H_2SO_4 + 3O_2$





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



### Absorbent

(a) Turpentine oil

(b) Oil of cinnamon

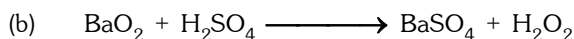
### Uses

(a) Sterilizing water

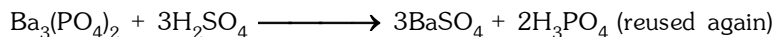
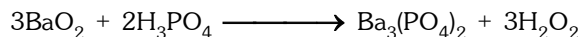
(b) Detection of position of the double bond in the unsaturated compound.

### 3. HYDROGEN PEROXIDE (H<sub>2</sub>O<sub>2</sub>)

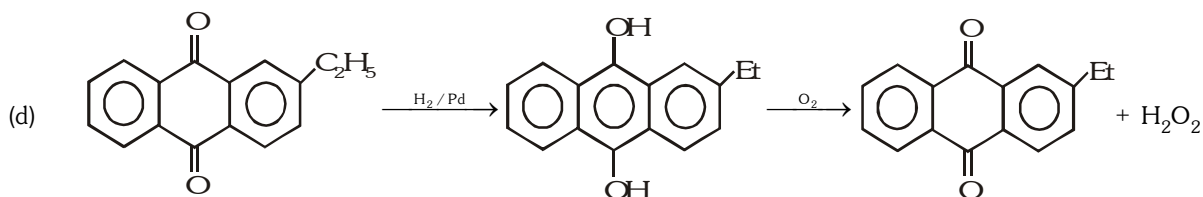
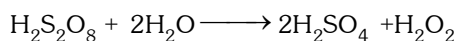
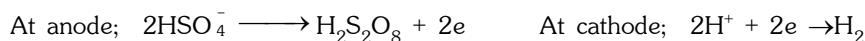
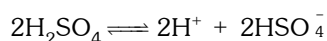
#### Preparation



Instead of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> is added now-a-days because H<sub>2</sub>SO<sub>4</sub> catalyses the decomposition of H<sub>2</sub>O<sub>2</sub> whereas H<sub>3</sub>PO<sub>4</sub> favours to restore it.



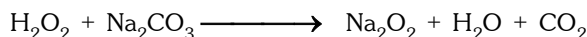
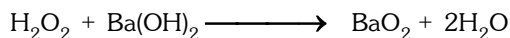
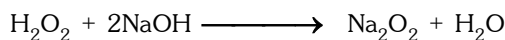
(c) Electrolysis of 50% H<sub>2</sub>SO<sub>4</sub> using high current density.



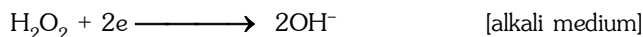
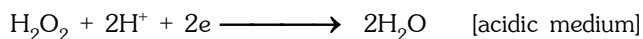
#### Properties

(a) Colourless, odourless liquid (B.P.152°C)

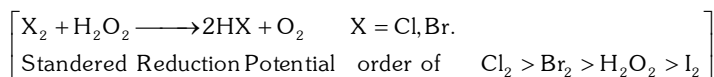
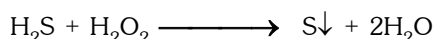
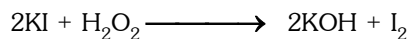
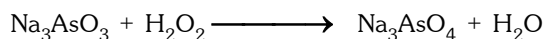
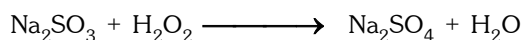
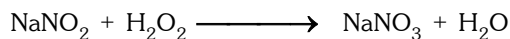
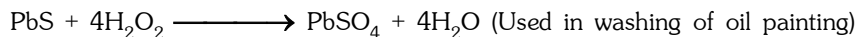
(b) **Acidic nature**

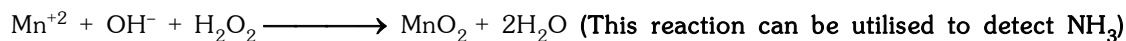
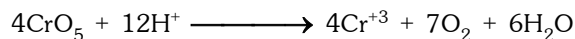
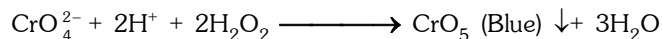
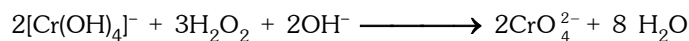
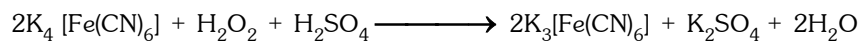
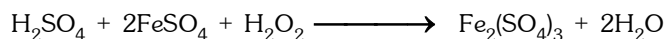


(c) **Oxidising and reducing nature**

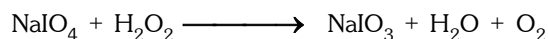
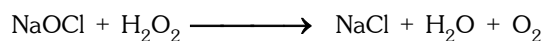
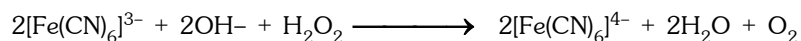
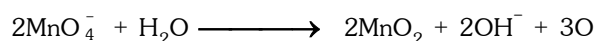
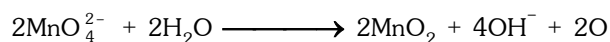
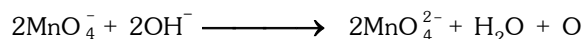
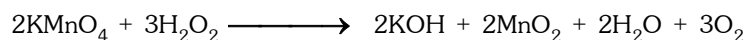
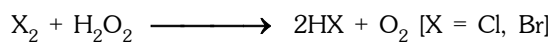
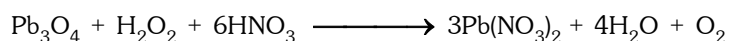
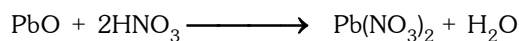
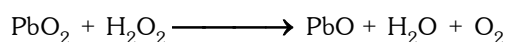
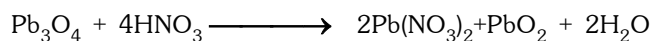
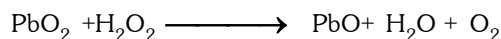
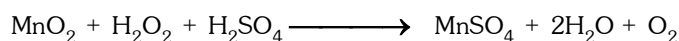
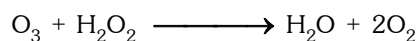
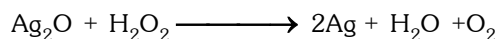


Oxidising nature



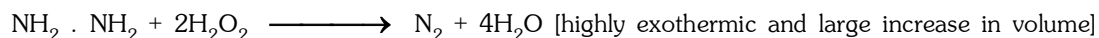


### Reducing nature

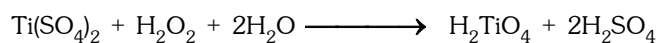


### Uses

- (a) As a rocket propellant



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

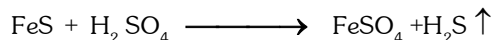


Pertitanic acid  
Yellow or orange

#### 4. HYDROGEN SULPHIDE (H<sub>2</sub>S) SULPHURATED HYDROGEN

##### Preparation

By the action of dil. HCl or H<sub>2</sub>SO<sub>4</sub> on iron pyrites.

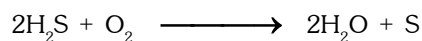


**Note :** The gas is then dried over fused CaCl<sub>2</sub> or P<sub>2</sub>O<sub>5</sub>. Conc. H<sub>2</sub>SO<sub>4</sub> cannot be used for drying purpose because H<sub>2</sub>S oxidize to sulphur.

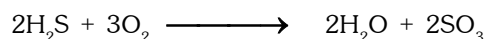
##### Properties

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

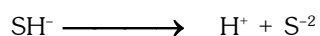
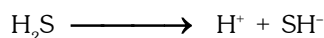
(a) It burn in air with blue flame



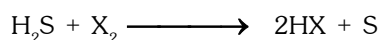
If the air supply is in excess



(b) It is a mild acid.



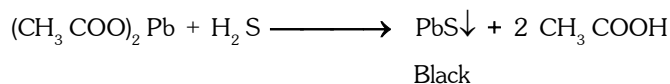
(c) It act as a reducing agent. It reduces halogen into corresponding hydroacid.



##### Tests of H<sub>2</sub>S

(a) Unpleasant odour resembling that of rotten eggs.

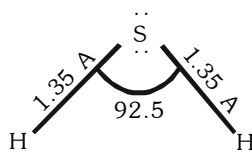
(b) It turns lead acetate into paper black



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

##### Structure of H<sub>2</sub>S

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



##### Uses

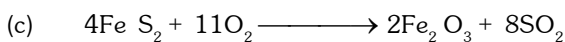
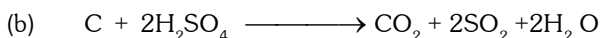
(a) It is mainly employed in salt analysis for the detection of cation.

(b) Reducing agent for H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, FeCl<sub>3</sub>

#### 5. SULPHUR DIOXIDE (SO<sub>2</sub>)

##### Preparation

Prepared by any of the following methods.

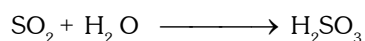


## Properties

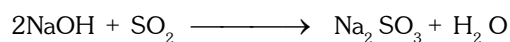
- (a) It has a pungent and suffocating odour.  
(b) It acts as lewis base due to presence of a lone pair of electrons.

(c) **Acidic nature**

It dissolves in  $H_2O$  to give sulphurous acid, hence known as sulphurous anhydride.

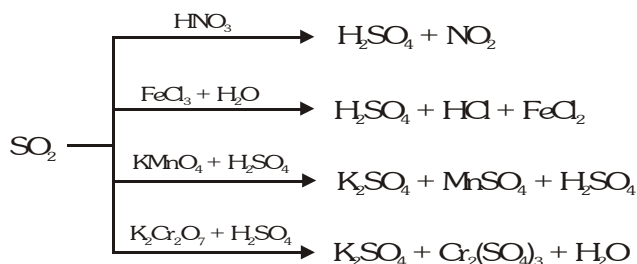


Due to acidic nature, it can react with bases to give salts.

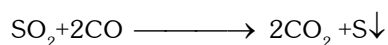
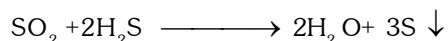


(d) **Reducing nature**

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

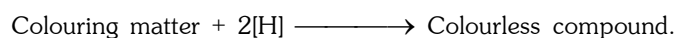
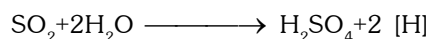


(e) **Oxidising nature**



(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.



- (ii) Since the colourless (reduced) compound is reoxidised by air to coloured compound, bleaching by  $SO_2$  is temporary.

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

## 6. SULPHURIC ACID $H_2SO_4$ (OIL OF VITRIOL)

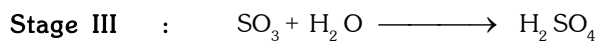
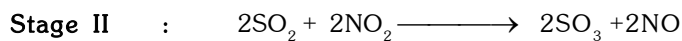
King of chemical (due to very great commercial importance)

### Preparation

$H_2SO_4$  is prepared by two methods

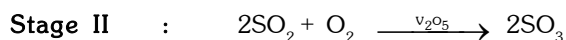
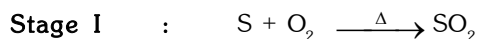
(a) **Lead chamber process**

The mixture containing  $SO_2$ , air & nitric oxide when treated with steam, sulphuric acid is formed.

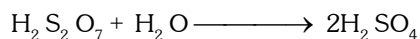


(b) **Contact process**

In this process  $\text{SO}_2$  is oxidised by air in the presence of catalyst (platinised asbestos).



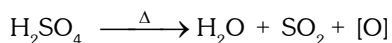
**Stage IV** : Sulphuric acid of any desired concentration can be obtained from oleum by dilution with water



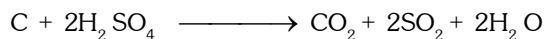
**Chemical properties**

(a) **As an oxidising agent**

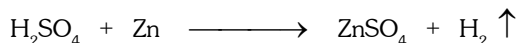
(i)  $\text{H}_2\text{SO}_4$  gives oxygen on strong heating, hot conc.  $\text{H}_2\text{SO}_4$  acts as an oxidising agent.



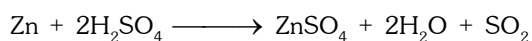
(ii) Non metals oxidised to their oxides.



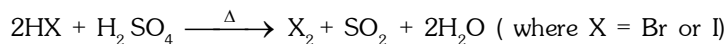
(iii) Dilute acid releases hydrogen with all metals except mercury, copper and noble metals.



Hot conc.  $\text{H}_2\text{SO}_4$  releases  $\text{SO}_2$  on reaction with metals.



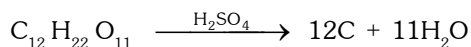
(iv) Oxidation of compounds



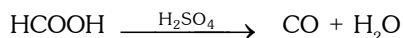
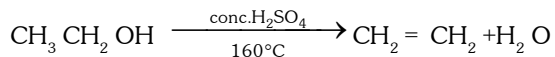
(b) **As a dehydrating agent**

(i) Conc.  $\text{H}_2\text{SO}_4$  is a powerful dehydrating agent. Its corrosive action on skin is due to dehydration of skin which then burns and produces itching sensation.

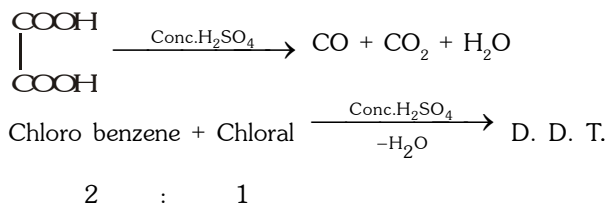
(ii) It's dehydrating property is due to strong affinity for water.



This is called as charring of sugar.





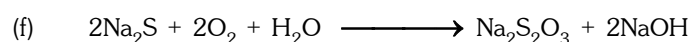
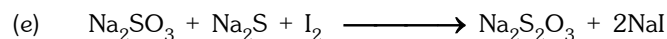
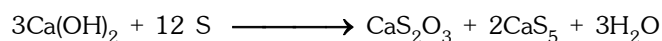
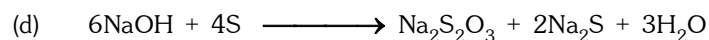
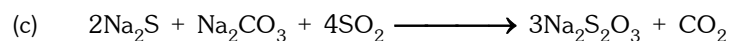
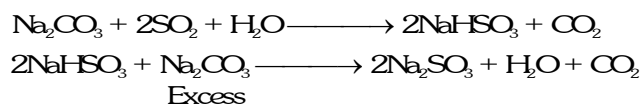
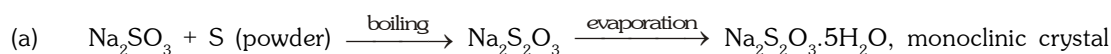


### Uses

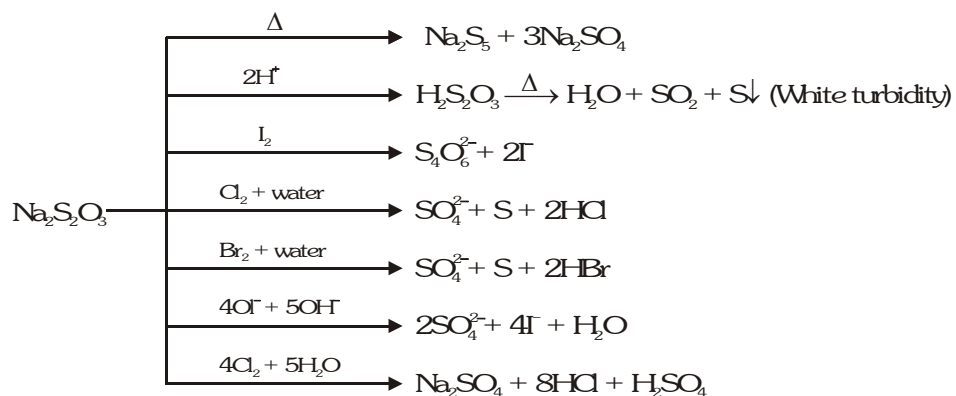
- In the manufacture of fertilisers like ammonium sulphate, calcium superphosphate etc.
- As a drying agent.

## 7. SODIUM THIOSULPHATE ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ )

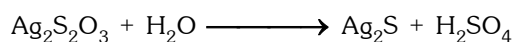
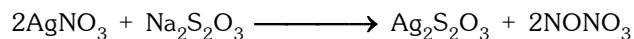
### Preparation



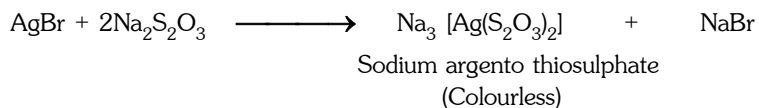
### Properties



**Action of  $\text{AgNO}_3$  :** A white precipitate of silver thiosulphate is obtained by the action of  $\text{AgNO}_3$  which changes to yellow, brown and finally black due to the formation of silver sulphide.

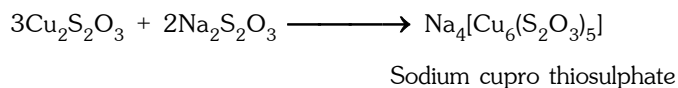
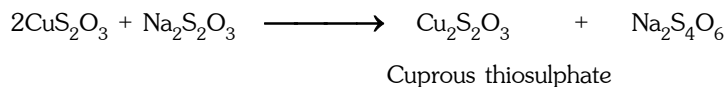
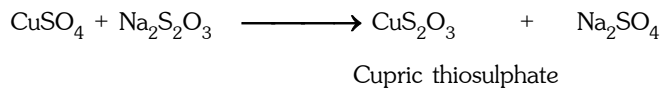


**Action of silver halides :** Halides form complexes with sodium thiosulphate. Silver bromide forms argento thiosulphate complex.



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  $\text{CuSO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ ,  $\text{Na}_3\text{AsO}_3$  etc.
- (e) Sodium hyposulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) is used for reducing indigo or other vat dyes.

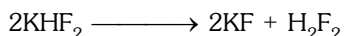
# HALOGEN FAMILY

## 1. FLUORINE (F<sub>2</sub>)

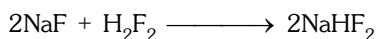
### Preparation

#### Moissan's method

Electrolyte is a [KHF<sub>2</sub> (1 part) and anhydrous H<sub>2</sub>F<sub>2</sub> (5 parts)]. 1 : 5 mixture of KHF<sub>2</sub> and anhydrous H<sub>2</sub>F<sub>2</sub>. The reaction taking place in this method are :



at anode ;  $2\text{F}^- \longrightarrow \text{F}_2 + 2\text{e}^-$       at cathode ;  $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$

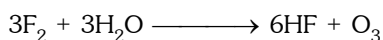
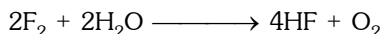


### Physical properties

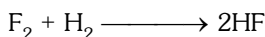
- Fluorine is a pale yellow gas which condenses to a clear yellow liquid having a density of 1.108 and B.P is  $-187.7^\circ\text{C}$ . At  $-223^\circ\text{C}$  it freezes to a pale yellow solid and at  $-252^\circ\text{C}$  the solid becomes colourless.
- It is a pungent smelling and poisonous gas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

### Chemical Properties

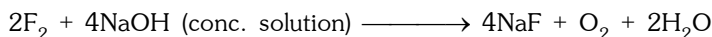
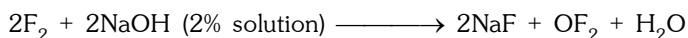
- Reaction with water** : Reaction is vigorous even in the dark giving O<sub>2</sub> and O<sub>3</sub>



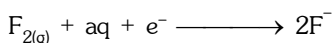
- Reaction with hydrogen** : F<sub>2</sub> combines with H<sub>2</sub> explosively even in the dark, forming HF.



- Action on alkalis** : Unlike Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub>, F<sub>2</sub> reacts with dil. alkalis (2% solution) and forms NaF and OF<sub>2</sub> (not NaFO). With conc. alkalis F<sub>2</sub> gives NaF and O<sub>2</sub> (not NaFO<sub>3</sub>).



- Oxidising property** : Since F<sub>2</sub> has the largest positive value of standard reduction electrode potential for the reduction reaction.



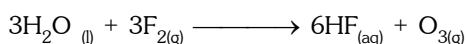
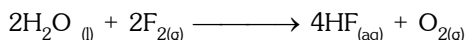
F<sub>2</sub> is the strongest oxidising agent among all the halogens. Maximum oxidising power of F<sub>2</sub> is confirmed by the following reactions -

- Action of F<sub>2</sub> on halides** : F<sub>2</sub> can liberate halogen from the aqueous solution of all the three halides (generally sodium or potassium halides) while other halogens cannot do so.

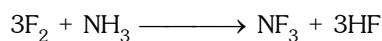
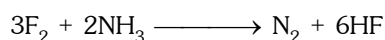


In the above reaction X<sup>-</sup> is oxidised to X<sub>2</sub>.

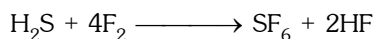
- Action of F<sub>2</sub> on H<sub>2</sub>O** : F<sub>2</sub> oxidises (decomposes) H<sub>2</sub>O to O<sub>2</sub> and O<sub>3</sub>



(e) **Action on NH<sub>3</sub>** : F<sub>2</sub> reacts with NH<sub>3</sub> to give N<sub>2</sub> and some NF<sub>3</sub>



(f) **Action on H<sub>2</sub>S**: H<sub>2</sub>S burns in an atmosphere of F<sub>2</sub>, forming SF<sub>6</sub> and HF

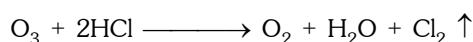
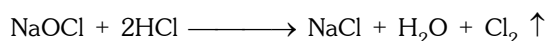
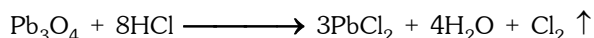
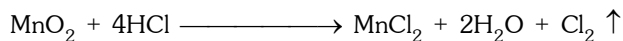
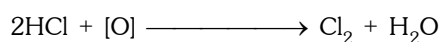


**Uses** : F<sub>2</sub> is used as an insecticide.

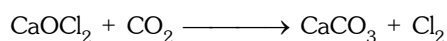
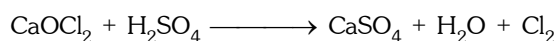
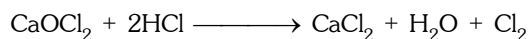
## 2. CHLORINE (Cl<sub>2</sub>)

### Preparation

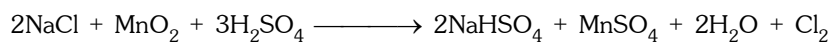
(a) **From HCl** : HCl is most important chemical to prepare chlorine and HCl reacts with a number of oxidising agents to liberate Cl<sub>2</sub>.



(b) **From bleaching powder** : Bleaching powder liberates Cl<sub>2</sub> when treated with mineral acid or CO<sub>2</sub>.

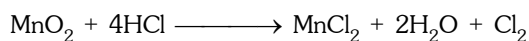


(c) **From chlorides** : Cl<sub>2</sub> may also be obtained by decomposing metal chlorides by MnO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>

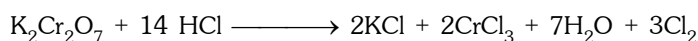
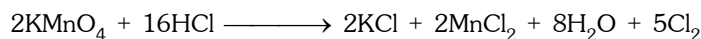


(d) **Laboratory method** : In laboratory, Cl<sub>2</sub> is prepared by action of HCl on MnO<sub>2</sub> or KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

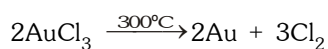
(i) **From MnO<sub>2</sub>**



(ii) **From K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or KMnO<sub>4</sub>**

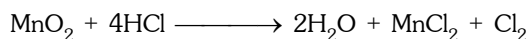


(iii) **Preparation of pure Cl<sub>2</sub>** : Cl<sub>2</sub> of high purity may be obtained by decomposing platinum chloride (PtCl<sub>4</sub>) or gold chloride (AuCl<sub>3</sub>)

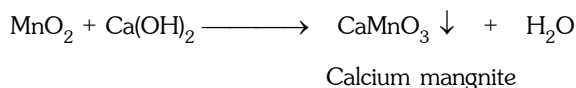
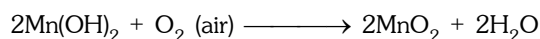
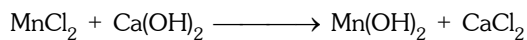


(iv) **Manufacturing**

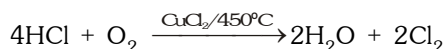
**Weldon's process** : This method involves the heating of pyrolusite (a mineral of Mn, contain  $\text{MnO}_2$ ) with conc. HCl.



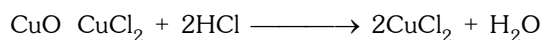
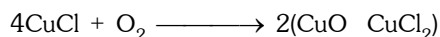
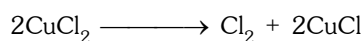
$\text{MnCl}_2$  thus obtained is also used for production of  $\text{Cl}_2$  by following process.



**Deacon's process** : In this method, HCl is oxidised by air in the presence of  $\text{CuCl}_2$  catalyst

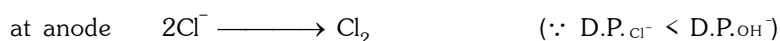
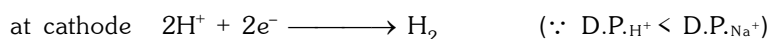
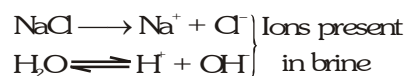


The probable mechanism of the reaction is as



Thus  $\text{Cl}_2$  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,  $\text{Cl}_2$  is liberated at anode.



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

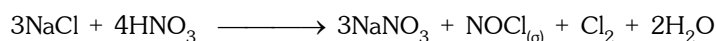
**By electrolysis of molten NaCl** : Electrolysis of molten NaCl gives  $\text{Cl}_2$  at anode and Na metal at cathode. This method of extraction of Na is known as Down's process. Down's cell is composed of:

- Anode : Steel rod
- Cathode : Graphite
- Electrolyte : Mixture of molten NaCl, and NaF
- Temperature :  $600^\circ\text{C}$

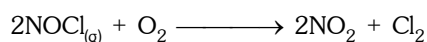
Following reactions take place in the cell



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



The gaseous mixture formed is also oxidised with oxygen.



The gaseous mixture is liquefied which on distillation gives  $\text{Cl}_2$

## Physical Properties

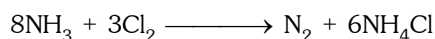
- (a) It is yellow green, pungent smelling, toxic gas. It has toxic effect on lungs, throat and nose.
- (b) It gives chlorine water when passed through water which is strong oxidation. If passed through ice cold water, crystals of  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$  are obtained.
- (c) On liquifaction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

## Chemical properties

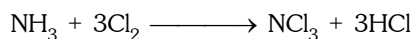


It reacts with ammonia under two conditions.

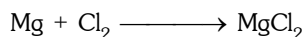
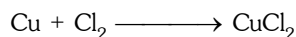
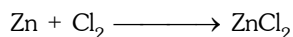
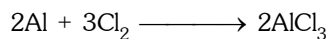
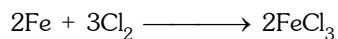
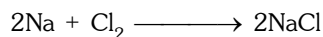
- (i) When ammonia in excess



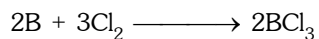
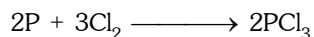
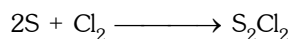
- (ii) When chlorine in excess



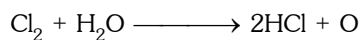
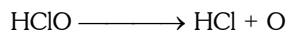
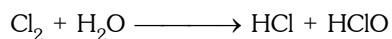
- (b) **Reaction with metals**



- (c) **Reaction with non metals**



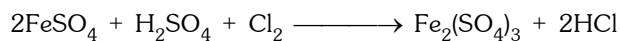
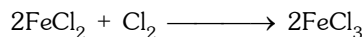
- (d) **Oxidising and bleaching nature**



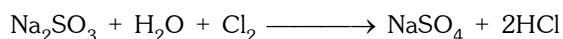
Coloured matter + (O)  $\longrightarrow$  Colourless matter

The bleaching action is permanent.

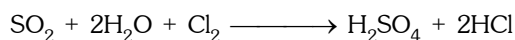
- (i) Ferrous chloride or ferrous sulphate containing dilute  $\text{H}_2\text{SO}_4$ , is oxidised to ferric chloride or ferric sulphate respectively.



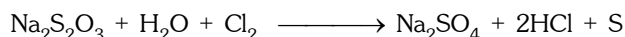
- (ii) Sulphites are oxidised to sulphates.



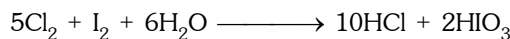
(iii) Moist sulphur dioxide is oxidised to  $\text{H}_2\text{SO}_4$



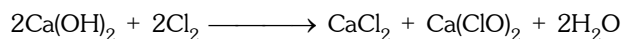
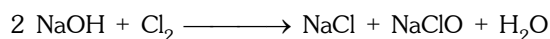
(iv) Sulphur is precipitated from sodium thiosulphate.



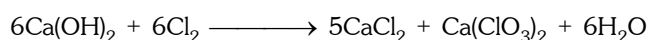
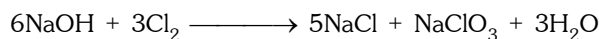
(v)  $\text{Cl}_2$  oxidises  $\text{I}_2$  to  $\text{HIO}_3$ .



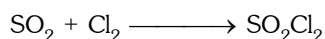
(e) **Action of alkalis** : When passed into cold dilute solution of alkalis, it forms chloride and hypochlorites.



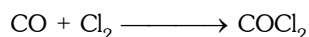
However with hot concentrated alkali solutions it forms chlorates.



(f) **Addition reactions** : Chlorine forms addition compounds with  $\text{SO}_2$ ,  $\text{CO}$  and unsaturated hydrocarbons.



Sulphuryl chloride



Carbonyl chloride (phosgene)



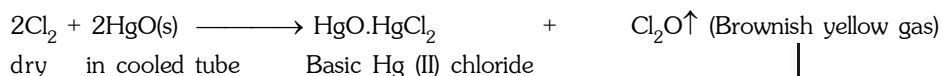
Ethylene chloride

### 3. OXIDES OF CHLORINE

+1	+4	+6	+7
$\text{Cl}_2\text{O}$	$\text{ClO}_2$	$\text{Cl}_2\text{O}_6$	$\text{Cl}_2\text{O}_7$
(Brownish yellow)	(Pale yellow)	(liq → dark red Solid → yellow)	Colourless solid

#### Dichloro oxide ( $\text{Cl}_2\text{O}$ )

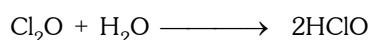
**Preparation** :  $\text{Cl}_2$  does not combine directly to produce its oxides but indirect method are there.



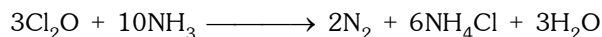
↓  
Condensed to orange liquid

#### Properties

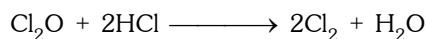
(a) It dissolves in water



(b) Explodes violently with  $\text{NH}_3$



(c) It is oxidising agent



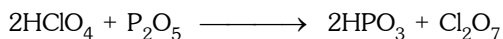




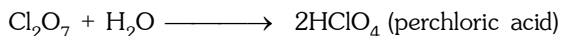
## Chlorine Heptoxide (Cl<sub>2</sub>O<sub>7</sub>)

It is the anhydride of HClO<sub>4</sub> and prepared from it by the reaction of P<sub>2</sub>O<sub>5</sub>

### Preparation



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

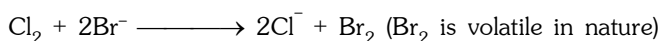


### Structure



## 4. BROMINE (Br<sub>2</sub>)

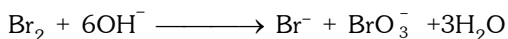
(a) **From Brine water :** Contains 65 ppm of Br<sup>-</sup>



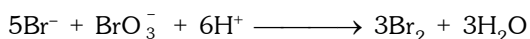
Hence it is collected by

(i) Removal of Br<sub>2</sub> vapour by steam of air.

(ii) Absorbing it into Na<sub>2</sub>CO<sub>3</sub> Solution

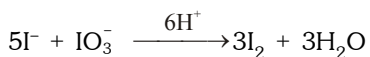


Then acidified to get pure Br<sub>2</sub>



## 5. IODINE (I<sub>2</sub>)

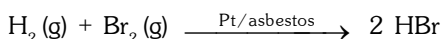
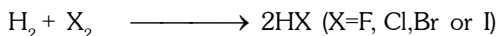
Chille salt petre contains traces of NaIO<sub>3</sub> which is reduced to I<sup>-</sup> by NaHSO<sub>3</sub>, then oxidation of I<sup>-</sup> to I<sub>2</sub> by IO<sub>3</sub><sup>-</sup>.



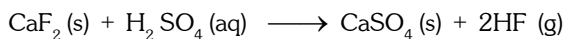
## 6. HALOGEN ACIDS

### Preparation

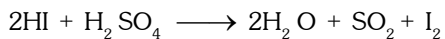
All the halogens combine directly with hydrogen to form halogen acids but their reactivity decreases progressively from fluorine to iodine.



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



H<sub>2</sub>SO<sub>4</sub> is not satisfactory for the preparation of HBr and HI because the HBr or HI formed are oxidised by H<sub>2</sub>SO<sub>4</sub> and the product is contaminated with the respective halogen. This difficulty can be overcome by using a non-oxidizing acid such as H<sub>3</sub>PO<sub>4</sub>.



### 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.  
 $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
- (d) **Thermal stability** : Thermal stability of the hydrides decreases from HF to HI i.e.  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$ . 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,  $(\text{HF})_n$  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.  $\text{HCl} > \text{HBr} > \text{HI} > \text{HF}$ .

### Chemical properties

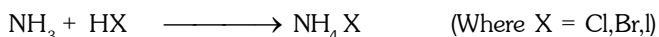
#### (a) Acidic Strength

- (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  $K_a$ .
- (iii) The acidic strength of halogen decreases from  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ .
- (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.

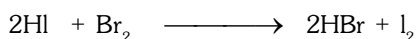
#### (c) Action of ammonia



White fumes

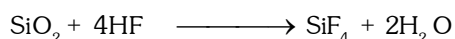
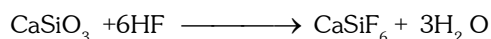
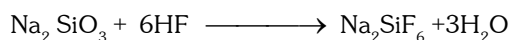
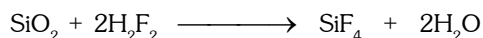
#### (d) Action of halogens

Chlorine is liberated from HCl only by fluorine  $\text{Br}_2$  is liberated from HBr by  $\text{Cl}_2$  and  $\text{F}_2$  only (not by  $\text{I}_2$ ).



## Abnormal Properties of HF

- Liquid at room temperature due to H bonding.
- Most thermal stable than other halogen hydrides.
- 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.
- HF form two type of salt ( $\text{NaHF}_2$ ,  $\text{Na}_2\text{F}_2$ )
- This acid attacks on silica of glass & formation of following compounds.



## 7. OXY ACID OF HALOGEN FAMILY

Name of the acids and their salts	Oxidation state of the halogen in the acid	Oxoacids			Structure	Stability	Acidic strength
		Cl	Br	I			
Hypohalous Hypohalite	+1	HClO	HBrO	HO	H-O-X	Decreases	Increases
Halous, Halites	+3	HClO <sub>2</sub>			H-O-X→O	Decreases	Increases
Halic, Halates	+5	HClO <sub>3</sub>	HBrO <sub>3</sub>	HO <sub>3</sub>	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{H-O-X} \end{array}$	Decreases	Increases
Perhalic, Perhalates	+7	HClO <sub>4</sub>	HBrO <sub>4</sub>	HO <sub>4</sub>	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{HO-X} \\ \downarrow \\ \text{O} \end{array}$	Decreases	Increases

**Acidity order :** HOX < HXO<sub>2</sub> < HXO<sub>3</sub> < HXO<sub>4</sub>

**Oxidising power :** HOX > HXO<sub>2</sub> > HXO<sub>3</sub> > HXO<sub>4</sub>

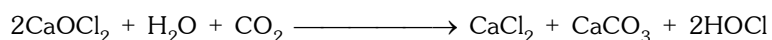
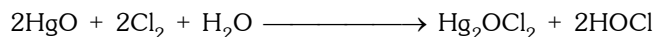
**Thermal stability :** HOX < HXO<sub>2</sub> < HXO<sub>3</sub> < HXO<sub>4</sub>

- Fluoric (I) acid (HOF) :** it is obtained when F<sub>2</sub> is passed over ice at 273 K.

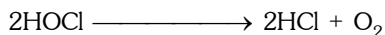


It is colourless unstable gas which decomposes to HF and O<sub>2</sub>. It is strong oxidising agent and oxidises H<sub>2</sub>O to H<sub>2</sub>O<sub>2</sub>.

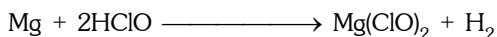
- Hypochlorous acid or chloric (I) acid (HOCl) :** It can be prepared by following reactions.



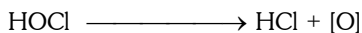
It is stable only in solution whose dilute solution is colourless while concentrated solution is yellow. It decomposes as



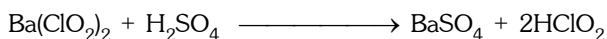
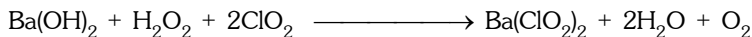
weak acid and with Mg it evolves  $\text{H}_2$



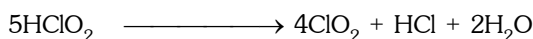
It is powerful bleaching and oxidising agent due to evolution of nascent oxygen.



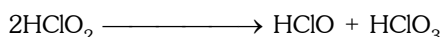
- (c) **Chlorous acid or chloric (III) acid ( $\text{HClO}_2$ )** : It is also known in aqueous solution and can be prepared by following reactions.



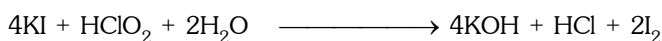
Its fresh solution is colourless but soon it turns yellow due to formation of  $\text{ClO}_2$



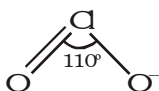
It shows disproportionation reaction as



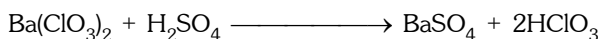
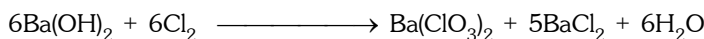
It liberates  $\text{I}_2$  from KI.



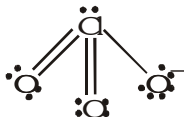
Its shape is angular with  $\text{sp}^3$  hybridised Cl-atom.



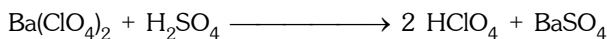
- (d) **Chloric acid ( $\text{HClO}_3$ )** : It is stable in aqueous solution only. It is prepared by action of conc.  $\text{H}_2\text{SO}_4$  on barium chlorate.



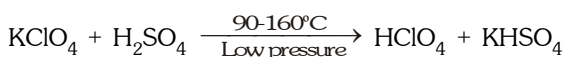
It is colourless pungent smelling liquid. It is stable in dark but decomposes in light. It acts as both oxidising and bleaching agent. Chlorate ion is pyramidal in geometry and central Cl-atom is  $\text{sp}^3$  hybridised.



- (e) **Perchloric acid ( $\text{HClO}_4$ )** : It is most stable among oxoacids of chlorine. It is prepared by following reaction.



In anhydrous form, it can be prepared by distillation of mixture of  $\text{KClO}_4$  and 96-97% of  $\text{H}_2\text{SO}_4$ .

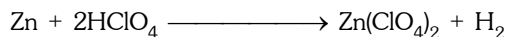


Anhydrous  $\text{HClO}_4$  is colourless oily liquid which turns dark on standing. If fumes in moist air.

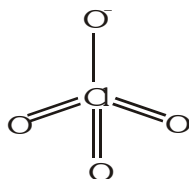
It is amongst strongest protonic acids known.



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



In  $\text{ClO}_4^-$ , central Cl-atom is  $\text{sp}^3$  hybridised and so its structure is tetrahedral.



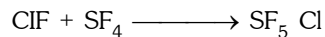
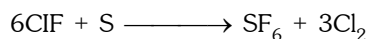
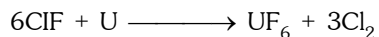
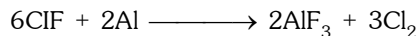
## 8. INTER HALOGEN

Types	AX	AX <sub>3</sub>	AX <sub>5</sub>	AX <sub>7</sub>
	ClF	ClF <sub>3</sub>	ClF <sub>5</sub>	IF <sub>7</sub>
	BrF	BrF <sub>3</sub>	BrF <sub>5</sub>	
	BrCl	(ICl <sub>3</sub> ) <sub>2</sub>	IF <sub>5</sub>	
	ICl	IF <sub>3</sub> (unstable)		
	IBr			
	IF (unstable)			

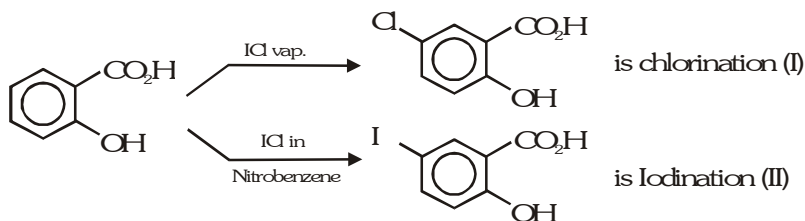
### Properties

- (i)  $\text{BrF}_5 + 3\text{H}_2\text{O} \longrightarrow \text{HBrO}_3 + 5\text{HF}$   
 (ii)  $\text{IF}_5 + 3\text{H}_2\text{O} \longrightarrow \text{HIO}_3 + 5\text{HF}$   
 (iii)  $\text{IF}_7 + \text{H}_2\text{O} \longrightarrow \text{IOF}_5 + 2\text{HF}$  less  
 $4\text{H}_2\text{O} \longrightarrow \text{HIO}_4 + 7\text{HF}$  } Parallel reaction

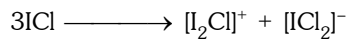
- (iv) ClF is highly reactive and as a fluorinating agent.



### One peculiarity with ICl



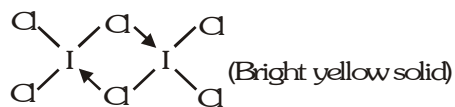
In  $\text{I}^{\text{nd}}$  case, the attacking species is  $\text{I}^+$  which has been supported by the formation of  $\text{I}^+$  in fused state as follows:



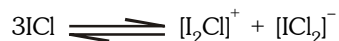
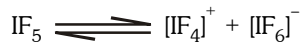
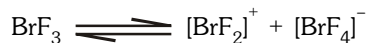
$\text{ICl}_3$  does not exist but its dimer exist.



Structure :

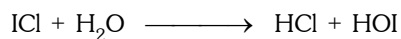


(v)  $I_2Cl_6$  : liquid has appreciable electrical conductivity like other interhalogens.



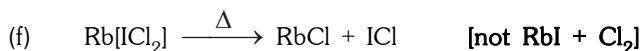
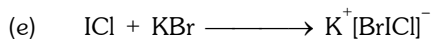
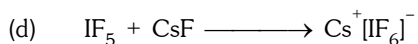
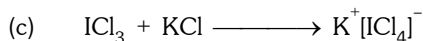
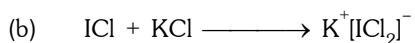
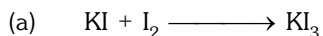
### Characteristics

- $5IF \longrightarrow IF_5 + 2I_2$  [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.
- $AX_5$  &  $AX_7$  type formed by large atoms like Br & I to accommodate more atoms around it.
- The interhalogens are generally more reactive than the halogens (except  $F_2$ ) due to weaker A-X bonds compared to X-X bonds.



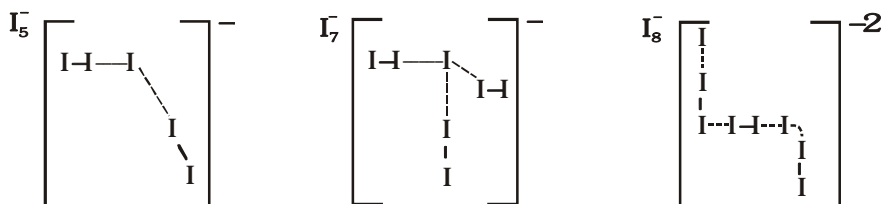
## 9. POLYHALIDES

### Preparation and properties



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

- Only  $F_3^-$  not known [due to absence of d-orbital] [i.e.  $Cs_2 I_3 - I_2 - I_3$ ]
- $I_3^-$ ,  $Br_3^-$ ,  $Cl_3^-$  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  $X_2$ .

<b>Anions</b>	<b>Acids</b>	<b>Dimer</b>
$CN^-$	HCN	$(CN)_2$
$SCN^-$	HSCN (thiocyanic acid)	$(SCN)_2$
$SeCN^-$		$(SeCN)_2$
$OCN^-$	HOCN (cyanic acid)	
$NCN^{2-}$ (Bivalent)	$H_2NCN$ (cyanamide)	
$ONC^-$	HONC (Fulminic acid)	
$N_3^-$	$HN_3$ (Hydrazoic acid)	

$CN^\ominus$  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  $ClCN$ ,  $BrCN$ ,  $ICN$  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 boiling 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 different noble gases are given below :

He	Ne	Ar	Kr	Xe	Rn
120	160	191	200	220	-

(f) The ionization energy values ( $\text{kJ mol}^{-1}$ ) for different noble gases are given below :

He	Ne	Ar	Kr	Xe	Rn
2372	2080	1520	1351	1170	1037

(g) The enthalpies of vaporization,  $\Delta H_{\text{vapour}}$  ( $\text{kJ mol}^{-1}$ ) 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)  $\frac{C_p}{C_v}$  for noble gases is 1.67.

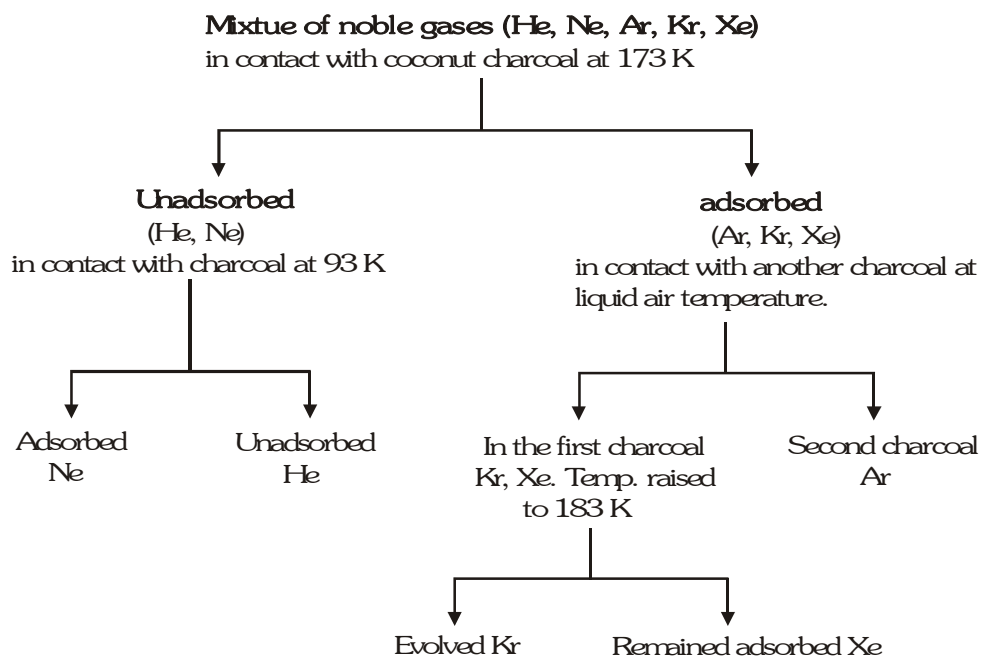
(i) The refractive index, dielectric constant and other physical properties of noble gases correspond to their monoatomic nature.

(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
He	0.0006	0.000037
Ne	0.0015	0.001
Ar	0.932	1.285
Kr	0.0001	0.00028
Xe	0.00001	0.00004



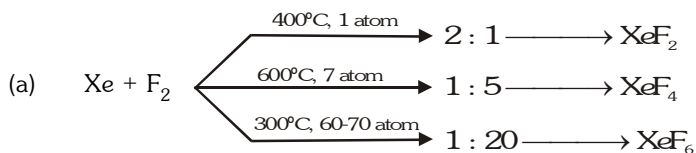
- (k) Helium is present to the extent of 2% in natural gas found in the united states and Canada.
- (l) Helium is also present in the minerals of radioactive elements uranium and thorium **Ex.** cleveite, uranite, thorianite, monazite, pitchblende etc.
- (m) The sixth member of the zero group was discovered 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 summarized below :



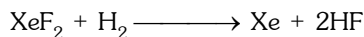
- (o) The viscosity of He is extremely low, about  $\frac{1}{100}$ th of hydrogen gas.
- (p) The thermal conductivity of He is very high about 800 times that of copper at room temperature
- (q) The lifting power of He is 92% that of hydrogen.
- (r) Helium is used for filling airships and balloons for meteorological observations.
- (s) Mixture of He with O<sub>2</sub> 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<sub>2</sub> 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

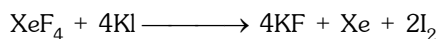
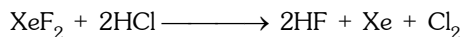
### Xenon fluorides



(b)  $\text{H}_2$  reduces Xe-fluorides to Xe

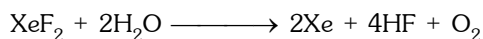


(c) Xe-fluorides oxidise  $\text{Cl}^-$  to  $\text{Cl}_2$  and  $\text{I}^-$  to  $\text{I}_2$

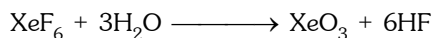
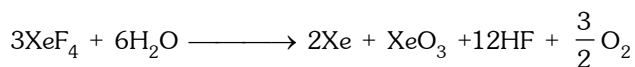


(d) **Hydrolysis**

$\text{XeF}_2$  reacts slowly with water



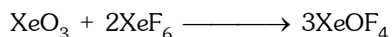
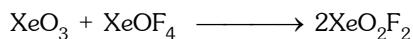
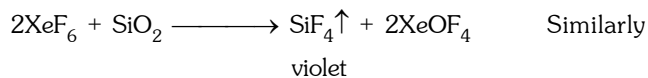
$\text{XeF}_4$  and  $\text{XeF}_6$  react violently with water giving  $\text{XeO}_3$



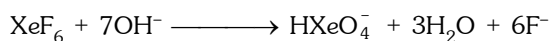
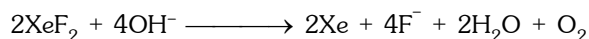
↓

(explosive, white hygroscopic solid)

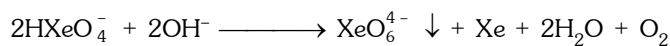
(e)  $\text{SiO}_2$  also converts  $\text{XeF}_6$  into  $\text{XeOF}_4$



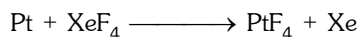
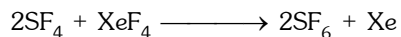
(f) Xe-fluorides are also hydrolysed in alkaline medium



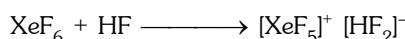
Xenate ion



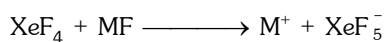
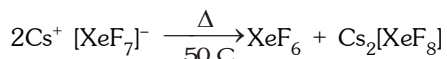
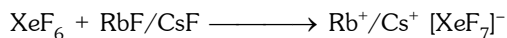
(g) They are used as fluorinating agent



(h) Act as a fluoride donor



(i) Act as Fluoride acceptor also



(alkali metals fluoride)