

---

## Fluorine – Occurrence and preparation :

- It is available in natural waters and also in sea water, soils, plants, bones and teeth.
- Its preparation is difficult because
  - (i) It attacks all containers and all materials
  - (ii) Anhydrous HF is a non – conductor
  - (iii) HF is highly stable and can not be easily oxidised to F<sub>2</sub>, since F<sub>2</sub> has the highest S.R.P.
  - (iv) Aq.HF is a good conductor but on electrolysis it gives H<sub>2</sub> and O<sub>2</sub> because give back HF and O<sub>2</sub>.

### Whytlaw Gray's method :

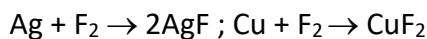
- The method is based on Moissan's principle.
- Electrolyte : Fused KHF<sub>2</sub>(KF + HF in 1 : 12 ratio )
- Electrolytic cell : Electrically heated copper vessel.
- Copper vessel cathode
- Anode : Graphite surrounded by copper diaphragm perforated at the bottom.
- Copper diaphragm prevents the mixing of H<sub>2</sub> and F<sub>2</sub>
- Fluorspar stoppers are used. Various parts are coated with Teflon to prevent corrosion.
- Products : At anode – F<sub>2</sub>  
At cathode – H<sub>2</sub>
- Reactions :  $\text{KHF}_2 \xrightarrow[700-1000^\circ\text{C}]{\text{fused}} \text{K}^+ + \text{H}^+ + 2\text{F}^-$   
 $2\text{F}^- \rightarrow \text{F}_2 + 2\text{e}^-$  (at anode)  
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  (at cathode)
- F<sub>2</sub> contains HF as impurity. HF is removed using NaF.  
 $\text{NaF} + \text{HF} \rightarrow \text{NaHF}_2$
- F<sub>2</sub> is almost pure with traces of HF

### Physical properties of F<sub>2</sub> :

- F<sub>2</sub> is pale yellow gas with pungent smell
- F<sub>2</sub> is heavier than air and poisonous in nature.
- F<sub>2</sub> form yellow liquid and yellow crystals.
- F<sub>2</sub> is diamagnetic

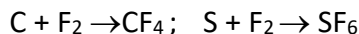
### Chemical properties of F<sub>2</sub>:

- F<sub>2</sub> is most reactive and hence it is called as super halogen.
    - 1) **with metals** : It reacts with all metals forming metal fluorides. It reacts with noble metals like Pt, Au, Ir also.
-



In cause of reaction between Cu and F<sub>2</sub>, the CuF<sub>2</sub> formed prevents further reaction between Cu and F<sub>2</sub>.

2) **with non – metals** : It reacts with all non – metals directly except O<sub>2</sub> and N<sub>2</sub>.

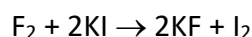
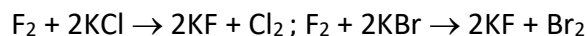


3) **with inert gases** : F<sub>2</sub> reacts with heavier inert gases like Kr and Xe.

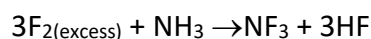


4) **with halides** : A lighter halogen or more electro-negative halogen displaces heavier halogen or less electronegative halogen from it's salts.

Thus F<sub>2</sub> displaces and oxidise all other halides ions to their respective halogens.

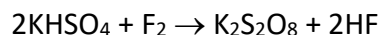


5) **with NH<sub>3</sub>** :  $3\text{F}_2 + 2\text{NH}_{3(\text{excess})} \rightarrow \text{N}_2 + 6\text{HF}$



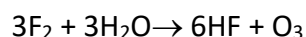
6) **with H<sub>2</sub>S** :  $4\text{F}_{2(\text{excess})} + \text{H}_2\text{S} \rightarrow \text{SF}_6 + 2\text{HF}$

7) **with KHSO<sub>4</sub>**: F<sub>2</sub> oxidises potassium bisulphate to potassium persulphate.



8)  $\text{CH}_4 + 4\text{F}_2 \rightarrow \text{CF}_4 + 4\text{HF}$

9) **with water** :  $2\text{F}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HF} + \text{O}_2$



### Uses of F<sub>2</sub>

- 1) In etching of glass HF is used (H<sub>2</sub>SiF<sub>6</sub> is formed)
  - 2) In Rocket fuels
  - 3) In separation of isotopes of Uranium by atmolysis
  - 4) SF<sub>6</sub> is used in high voltage electricity
  - 5) NaF and Na<sub>3</sub>AlF<sub>6</sub> are used as insecticides
  - 6) Like DDT, DDFT is used as fungicide
  - 7) Freon (CCl<sub>2</sub>F<sub>2</sub>) is used in refrigeration
  - 8) Teflon, [(C<sub>2</sub>F<sub>4</sub>)<sub>n</sub>] is used as anticorrosive plastic
-

---

## Chlorine :

- It is available as chlorides in nature.
- In sea water 2.5 % NaCl is present by weight.

### Minerals :

- 1) Rock salt : NaCl
- 2) Horn silver : AgCl
- 3) Sylvine : KCl
- 4) Carnallite :  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

**Preparation of  $\text{Cl}_2$ :** It was prepared by scheele laboratory preparation : Oxidation of HCl with  $\text{MnO}_2$



- **Industrial preparation :**
  - **1. Down's process :** It involves electrolysis of fused NaCl electrolyte : fused NaCl
  - electrolytic cell : Iron \ steel tank
  - Anode : Carbon rod
  - Cathode : Iron
  - Products at cathode and anode : Na and  $\text{Cl}_2$
  - Addition of little amounts of  $\text{CaCl}_2$ , KCl, KF : To decrease M.P. of NaCl
  - 
  - Possible impurity : Ca, To reduce fuel wastage , To reduce chances of burning Na
  - Iron wire guase : prevents mixing of Na and  $\text{Cl}_2$  : To reduce dissolution of Na in electrolyte.
  - **Nelson's cell method :** It involves electrolysis of brine solution
  - **Electrolyte : aqueous NaCl**
  - Electrolytic cell : Iron tank
  - Anode : Graphite rod
  - Cathode : Iron tank
  - Asbestos lining : Separates anode from cathode
  - Product at anode :  $\text{Cl}_2$
  - Products at cathode:  $\text{H}_2$ , NaOH
  - Passage of steam : To keep the solution hot and clear the pores
  - Possible impurities in NaOH: NaCl, NaOCl,  $\text{NaClO}_3$
-

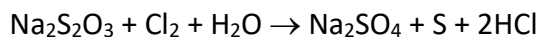
---

### Physical properties of Cl<sub>2</sub> :

- It is greenish yellow, pungent smelling gas
- It is poisonous and affects mucous membrane
- It causes head ache and man prove fatal in large quantities
- It condenses to yellow liquid and then to yellow solid.
- It is about 2.5 times heavier than air.

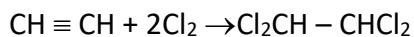
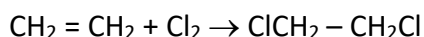
### Chemical properties of Cl<sub>2</sub>:

- 1) **with metals** : It reacts with almost all metals at room temperature.  
Highest metal chloride is generally formed rather than lower metal chloride  
$$\text{Cu} + \text{Cl}_2 \rightarrow \text{CuCl}_2$$
$$2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3$$
  - 2) **with non metals** : It directly combines with many non – metals like H<sub>2</sub>, P, S etc.
  - 3) **with H<sub>2</sub>O** : It dissolves in H<sub>2</sub>O to give chlorine water. Chlorine water consists of HCl and HOCl. on long standing HOCl decomposes to liberate O<sub>2</sub> and only HCl is left.
  - 4) **with alkalies** :
    - i) with cold alkalies, Cl<sub>2</sub> forms hypochlorites  
$$\text{Cl}_2 + \text{NaOH} \rightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}$$
    - ii) with hot alkalies, Cl<sub>2</sub> form chlorates  
$$3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$$
  - 5) **with halides** : It displaces bromine and iodine from their respective salt solutions  
$$2\text{KBr} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{Br}_2$$
$$2\text{KI} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{I}_2$$
  - 6) **with NH<sub>3</sub>** : 
$$\text{NH}_3 + 3\text{Cl}_{2(\text{excess})} \rightarrow \text{NCl}_3 + 3\text{HCl}$$
$$8\text{NH}_{3(\text{excess})} + 3\text{Cl}_2 \rightarrow 6\text{NH}_4\text{Cl} + \text{N}_2 \uparrow$$
  - 7) **Formation of addition compounds with SO<sub>2</sub>, CO, NO** :  
$$\text{CO} + \text{Cl}_2 \xrightarrow{\text{sun light}} \text{COCl}_2 \text{ (phosgene)}$$
$$2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl} \text{ (Nitrosyl chloride)}$$
$$\text{SO}_2 + \text{Cl}_2 \rightarrow \text{SO}_2\text{Cl}_2 \text{ (Sulphuryl chloride)}$$
  - 8) **Oxidising nature**: It is a strong oxidising agent.  
Moist Cl<sub>2</sub> bleaches vegetable coloring matter by it's oxidising nature.
    - i) It oxidises ferrous to ferric  
$$2\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3$$
    - ii) It oxidises hydrogen sulphide to sulphur  
$$\text{H}_2\text{S} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{S}$$
    - iii) It oxidises sulphite / thiosulphate into sulphate  
$$\text{Na}_2\text{SO}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$$
-

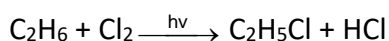
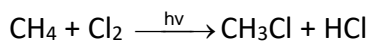


**9) with hydrocarbons :**

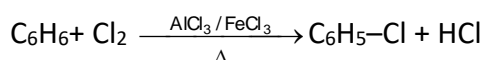
i) addition to unsaturated d :



ii) substitution in saturated :



iii) Substitution in Benzene:



**Uses of  $\text{Cl}_2$  :**

- As disinfectant
  - In sterilization of drinking water
  - In extraction of metals like Au, Pt
  - As bleaching agent for wood pulp. Rayon, cotton
  - In the preparation of solvents like  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ , Weston, Westrosol.
  - In the preparation of insecticides like DDT.
  - In plastics and rubber
  - In the preparation of poisonous gases like mustard gas phosgene, teargas etc.
-