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_2, since F_2 has the highest S.R.P.
  (iv) Aq.HF is a good conductor but on electrolysis it gives H_2 and O_2 because give back HF and O_2.

Whytlaw Gray's method :

- The method is based on Moissan's principle.
- Electrolyte : Fused KHF_2(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_2 and F_2
- Fluorspar stoppers are used. Various parts are coated with Teflon to prevent corrosion.
- Products : At anode – F_2
  At cathode – H_2
- Reactions : $KHF_2 \xrightarrow[700-1000^\circ C]{\text{fused}} K^+ + H^+ + 2F^-$
  $2F^- \rightarrow F_2 + 2e^-$ (at anode)
  $2H^+ + 2e^- \rightarrow H_2$ (at cathode)
- F_2 contains HF as impurity. HF is removed using NaF.
  $NaF + HF \rightarrow NaHF_2$
- F_2 is almost pure with traces of HF

Physical properties of F_2 :

- F_2 is pale yellow gas with pungent smell
- F_2 is heavier than air and poisonous in nature.
- F_2 form yellow liquid and yellow crystals.
- F_2 is diamagnetic

Chemical properties of F_2:

- F_2 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.

$Ag + F_2 \rightarrow 2AgF$; $Cu + F_2 \rightarrow CuF_2$

In cause of reaction between Cu and F_2, the CuF_2 formed prevents further reaction between Cu and F_2.

2) **with non – metals :** It reacts with all non – metals directly except O_2 and N_2.

$C + F_2 \rightarrow CF_4$; $S + F_2 \rightarrow SF_6$

3) **with inert gases :** F_2 reacts with heavier inert gases like Kr and Xe.

Compounds of Xe and F_2 : XeF_2, XeF_4, XeF_6

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

Thus F_2 displaces and oxidise all other halides ions to their respective halogens.

$F_2 + 2KCl \rightarrow 2KF + Cl_2$; $F_2 + 2KBr \rightarrow 2KF + Br_2$

$F_2 + 2KI \rightarrow 2KF + I_2$

5) **with NH_3 :** $3F_2 + 2NH_{3(excess)} \rightarrow N_2 + 6HF$

$3F_{2(excess)} + NH_3 \rightarrow NF_3 + 3HF$

6) **with H_2S :** $4F_{2(excess)} + H_2S \rightarrow SF_6 + 2HF$

7) **with $KHSO_4$**: F_2 oxidises potassium bisulphate to potassium persulphate.

$2KHSO_4 + F_2 \rightarrow K_2S_2O_8 + 2HF$

8) $CH_4 + 4F_2 \rightarrow CF_4 + 4HF$

9) **with water :** $2F_2 + 2H_2O \rightarrow 4HF + O_2$

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

Uses of F_2

1) In etching of glass HF is used ($H_2SiF_6$is formed)
2) In Rocket fuels
3) In separation of isotopes of Uranium by atmolysis
4) SF_6 is used in high voltage electricity
5) NaF and Na_3AlF_6 are used as insecticides
6) Like DDT, DDFT is used as fungicide
7) Freon (CCl_2F_2) is used in refrigeration
8) Teflon, $[(C_2F_4)_n]$ 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 : $KCl.MgCl_2.6H_2O$

Preparation of Cl_2: It was prepared by scheele laboratory preparation : Oxidation of HCl with MnO_2

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

- **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 Cl_2
- Addition of little amounts of $CaCl_2$, KCl, KF : To decrease M.P. of NaCl
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- Possible impurity : Ca, To reduce fuel wastage , To reduce chances of burning Na
- Iron wire guase : prevents mixing of Na and 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 : Cl_2
Products at cathode: H_2, NaOH
Passage of steam : To keep the solution hot and clear the pores
Possible impurities in NaOH**:** NaCl, NaOCl,$NaClO_3$

Physical properties of Cl_2 :

- 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_2:

- 1) **with metals** : It reacts with almost all metals at room temperature.
  Highest metal chloride is generally formed rather than lower metal chloride
  $Cu + Cl_2 \rightarrow CuCl_2$
  $2Fe + 3Cl_2 \rightarrow 2FeCl_3$
- 2) **with non metals** : It directly combines with many non – metals like H_2, P, S etc.
- 3) **with H_2O** : It dissolves in H_2O to give chlorine water. Chlorine water consists of HCl and HOCl. on long standing HOCl decomposes to liberate O_2 and only HCl is left.

4) **with alkalies** :

i) with cold alkalies, Cl_2 forms hypochlorites
$Cl_2 + NaOH \rightarrow NaCl + NaOCl + H_2O$

ii) with hot alkalies, Cl_2 form chlorates
$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

5) **with halides** : It displaces bromine and iodine from their respective salt solutions
$2KBr + Cl_2 \rightarrow 2KCl + Br_2$
$2KI + Cl_2 \rightarrow 2KCl + I_2$

6) **with NH_3** : $NH_3 + 3Cl_{2(excess)} \rightarrow NCl_3 + 3HCl$
$8NH_{3(excess)} + 3Cl_2 \rightarrow 6NH_4Cl + N_2\uparrow$

7) **Formation of addition compounds with SO_2, CO, NO :**
$CO + Cl_2 \xrightarrow{\text{sun light}} COCl_2$ (phosgene)
$2NO + Cl_2 \rightarrow 2NOCl$ (Nitrosyl chloride)
$SO_2 + Cl_2 \rightarrow SO_2Cl_2$ (Sulphuryl chloride)

8) **Oxidising nature:** It is a strong oxidising agent.
Moist Cl_2 bleaches vegetable coloring matter by it's oxidising nature.

i) It oxidises ferrous to ferric
$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$

ii) It oxidises hydrogen sulphide to sulphur
$H_2S + Cl_2 \rightarrow 2HCl + S$

iii) It oxidises sulphite / thiosulphate into sulphate
$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$

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

9) **with hydrocarbons :**

i) addition to unsaturated d :

$CH_2 = CH_2 + Cl_2 \rightarrow ClCH_2 - CH_2Cl$

$CH \equiv CH + 2Cl_2 \rightarrow Cl_2CH - CHCl_2$

ii) substitution in saturated :

$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$

$C_2H_6 + Cl_2 \xrightarrow{hv} C_2H_5Cl + HCl$

iii) Substitution in Benzene:

$C_6H_6 + Cl_2 \xrightarrow[\Delta]{AlCl_3 / FeCl_3} C_6H_5{-}Cl + HCl$

Uses of 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 CCl_4, $CHCl_3$, $C_2H_4Cl_2$, 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.