12. GROUP 17 ELEMENTS (VII A GROUP ELEMENTS)

Synopsis :

F, Cl, Br, I and At constitute the VII A group in periodic table.

- According to IUPAC convention, their group number is 17
- They are p – block elements and their outer shell configuration is $ns^2\ np^5$.
- The list of element is

Element	Period	Symbol	A.t.No	Electronic configuration
Fluorine	2	F	9	$[He]2s^2 2p^5$ (or) 2, 7
Chlorine	3	Cl	17	$[Ne]3s^2\ 3p^5$ (or) 2,8,7
Bromine	4	Br	35	$[Ar]3d^{10}4s^2 4p^5$ (or) 2, 8, 18, 7
Iodine	5	I	53	$[Kr]\ 4d^{10}\ 5s^2\ 5p^5$ (or) 2, 8, 18, 18, 7
Astatine	6	At	85	$[Xe]4f^{14}5d^{10}6s^2\ 6p^5$ (or) 2, 8,18,32,18,7

- Astatine is radioactive element
- F_2, Cl_2, Br_2, I_2 are known as halogens. Halogen means "Produced in the form of sea salt".
  e.g. Sea water has NaCl, $MgCl_2$, $MgBr_2$, $NaIO_3$.
- All halogens occur only in combined state. Fluorine occurs mostly as fluorspar (CaF_2) and fluorapatite $3Ca_3(PO_4)_2.CaF_2$
- The are the most electro negative elements.

General characteristics and group trends :

- Density, mp, bp, bond length, vander Waal's forces of attractions and intensity of the colour of the halogens increase down the group.
- IP_1, EN, volatility, solubility in water, standard reduction potential value and non-metallic character decrease down the group.
- IP_1 of F is very high because of its small size.
- F is most electro negative element. In Paulig's scale EN of F is 4.0.
- F_2, Cl_2 are gases. Br_2 is liquid. I_2 is solid. The change in physical state is due to the increase in the vander Waal's force between the molecules down the group which is due to increase in molecular weight.
- The order of EA is Cl > F > Br > I.
- The low EA value of F is due to interelectronic repulsions and due to the small size of F atom.
  The incoming electron experience greater repulsions due to high electron density in 2 p sub level.
- The order of bond energies is $Cl_2 > Br_2 > F_2 > I_2$
- F_2 is highly reactive because of its low bond energy.
- Mulliken proposed multiple bonding in Cl_2, Br_2, I_2 with p – d combination. F atom has no d – orbitals. So, multiple bond formation in F_2 is not possible and is the reason for the low BE of F_2.
- Coulson suggested that in F_2, the LP electrons of one atom repel the LP electrons of second F atom because of short F – F distance. High inter nuclear repulsions and inter electronic repulsions are also responsible for its low BE value.

- Of the two explanations, Coulson's view is widely accepted.

  Halogens are coloured.

  - The colour of halogen is due to the absorption and transmission of light in visible region.
  - Transmitted light is the complementary colour of the absorbed light.
  - Absorbed light makes electron to promote from ground state to higher energetic states.
  - As the size of the halogen atom increases, excitation energy of the electron decreases.
  - F absorbs high energetic violet light and transmits low energetic yellow light. Yellow colour is the complementary colour to violet light.
  - I absorbs low energetic yellow light and transmits violet light.
  - F_2 has pale yellow colour
  - Cl_2 is greenish yellow in colour
  - Br_2 has orange red colour
  - I_2 is violet in colour

Oxidation States :

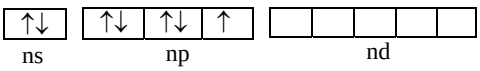
- F exhibits only –1 oxidation state in its compounds since it is the most electro – ve atom the valency of F can not be more than one due to the absence of vacant d- orbitals in valence shell.
- Cl, Br, I exhibit – 1, + 1, + 3 + 5 + 7 oxidation states because they are less electronegative and contain vacant d –orbitals in their valence shells.

  –1, + 1 oxidation states are possible with ground state configuration.

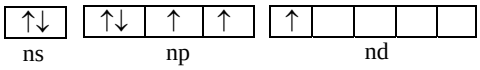
  + 3, + 5, + 7 oxidation states are possible with excited state configuration.

  +ve oxidation states are seen in only covalent compounds.
- Higher oxidation states are found is interhalogen compounds, oxides and oxo acids.

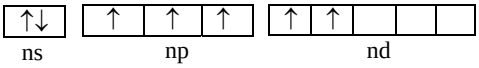
  (a) Ground state configuration of halogen atom is



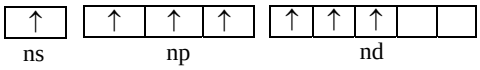
  (b) 1st excited state configuration is



  (c) 2nd excited state configuration is



  (d) 3rd excited state configuration is



- Inter halogen compounds are formed when one halogen combines with another halogen.
- In interhalogen compounds, π bonds are not formed by the halogen atom.

SNO	Interhalogen compound	Configuration	Hybridisation	O.S. of X	No.of bonds	Shape
(i)	XA	(a)	No hybridisation	+ 1	1	Linear
(ii)	XA_3	(b)	sp^3d	+ 3	3	Trigonal bipyramidal with 2 LP (or) trigonal pyramidal (or) T –shape
(iii)	XA_5	(c)	sp^3d^2	+ 5	5	Octahedral with 1 LP (or) square pyramidal
(iv)	XA_7	(d)	sp^3d^3	+ 7	7	Pentagonal bipyramidal

- *Note :* In all above molecules X is the central halogen atom which is less electronegative and A is more electronegative halogen atom.

Oxidising power :

- All the halogens are oxidising agents. Their oxidising power is high due to high EA values.
  The order of oxidising power is $F_2 > Cl_2 > Br_2 > I_2$
  The order of S.R.P is $F_2 > Cl_2 > Br_2 > I_2$
- All S.R.P. values are +ve. S.R.P. is a measure of the ability to undergo reduction.
- Oxidising ability of halogens depends on the net energy change of the process, $\frac{1}{2}X_{2(s)} \rightarrow X^-_{(aq)}$
- The net energy change is calculated using Born- Haber cycle (or) Hess law.
  $\Delta H_1 + X_{2(s)} \rightarrow X_{2(l)}$ ΔH_1 =Enthalpy of fusion
  $\Delta H_2 + X_{2(l)} \rightarrow X_{2(g)}$ ΔH_2=Enthalpy of vapourisation
  $\frac{1}{2}D + \frac{1}{2}X_{2(g)} \rightarrow X_{(g)}$ Δ = Enthalpy of dissociation
  $e + X_{(g)} \rightarrow X^-_{(g)} + E$ E = Electron affinity
  $aq + X^-_{(g)} \rightarrow X^-_{(aq)} + \Delta H_3$ ΔH_3=Enthalpy of hydration
- The net energy change of the process, $\frac{1}{2}X_{2(s)} \rightarrow X^-_{(aq)}$ is $\left(E + \Delta H_3 - \frac{\Delta H_1}{2} - \frac{\Delta H_2}{2} - \frac{D}{2}\right)$
- Greater this value, greater is the oxidising capacity of the halogen.
- Higher oxidising capacity of F_2 is due to
  (i) Low enthalpy of dissociation of F – F due to the weakness of F – F bond
  (ii) High enthalpy of hydration of F^- due to its small size.

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 : $KHF_2 \xrightarrow[700-1000°C]{\text{fused}} K^+ + H^+ + 2F^-$
  $2F^- \rightarrow F_2 + 2e^-$ (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
- 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.

OXY ACIDS OF CHLORINE:

OXYACIDS	FORMULA	OXIDATION STATE
Hypochlorous acid	HClO or HOCl	+1
Chlorous acid	$HClO_2$	+3
Chloric acid	$HClO_3$	+5
Percloric acid	$HClO_4$	+7

- Cl - O bond length decreases from OCl^- to ClO_4^-
- Cl - O bond energy increases from OCl^- ClO_4^- to except for ClO_3^-
- **HYPOCHLOROUS ACID:**
- Chlorine atom in ClO^- ion is sp^3 hybridised with lone pair electrons.
- ClO^- ion is stable due to strong tendency to form Pp - dp bonding between filled P-orbitals of oxygen and vacant d-orbitals of chlorine.
- Between one oxygen atom and chlorine atom there is σ bond

CHLOROUS ACID:

- Chlorine atom in ClO_2^- ion is sp^3 hybridised with two lone electron pairs.
- The shape of ClO_2^- ion is angular
- ClO_2^- ion contains 2σ and one π bonds.
- The bond angle is 111^o

CHLORIC ACID:

- Chlorine atom in ClO_3^- ion is sp^3 hybridised with one lone electron pair.
- The shape of ClO_3^- ion is pyramidal.
- ClO_3^- ion contains 3σ and 2π bonds.
- In ClO_3^- ion O-Cl-O bond angle is 106^θ

PERCHLORIC ACID:

- Chlorine atom in ClO_4^- ion is sp^3 hybridised with no lone pair electrons.

- The shape of ClO_4^- ion is tetrahedral.
- ClO_4^- ion contains 4σ and 3π bonds.
- The O-Cl-O bond angle is $109^0 28`$.
- Perchloric acid is dimerized due to hydrogen bond.

STRUCTURAL PARAMETERS OF OXOACIDS OF CHLORINE

Acid	Cl - O *distance* (A°)	$\angle OClO$ *in the anion*	Cl-O bond energy in $kj\,mol^{-1}$
HClO	1.70	–	209
$HClO_2$	1.64	111°	245
$HClO_3$	1.57	106°	244
$HClO_4$	1.45	109.5°	364

- **Bleaching powder (or) Chloride of lime, $CaOCl_2$ (or) Ca(OCl) Cl.**
- It is a mixture of $CaCl_2$ and $Ca(OCl)_2$ (calcium hypochlorite)
- It is also called calcium chloro hypochlorite or calcium oxychloride.

Manufacture :

- It is manufactured in Bachmann's plant.
- Cl_2 gas is passed into dry slaked lime

  $Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$
- The plant is a vertical cast iron tower
- It has two inlets, one for hot air just above the base, second inlet is for Cl_2 just above the 1st inlet.
- Hopper is arranged at the top for sending slaked lime.
- Exit is arranged just blow the hopper for the escape of unused Cl_2 and air.
- Horizontal shelves with rotating rakes are arranged at regular heights.
- Dry slaked lime moves downwards with the help of rotating rakes and Cl_2 moves up.
- $CaOCl_2$ is formed based on the "principle of counter currents".
- Principle of counter currents means reactants will react by moving.
- Hot air drives away unreacted chlorine.

Physical properties :

- Yellowish white powder with smell of chlorine
- Most of it is soluble in water but a small amount of insoluble lime.
- **Chemical properties :**
- Reactions of bleaching powder are

  i) with insufficient and excess dilute acid

  ii) auto oxidation

  iii)catalytic decomposition

  iv)with cold and hot water

  v) oxidation of lead salts and ethyl alcohol

(i) A. with insufficient dilute acid : It first forms HOCl and finally releases O_2.

$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + CaCl_2 + 2HCl + O_2$

It is good oxidising agent at is liberates nascent oxygen.

B. with excess of dilute acid :

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

$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$

The released Cl_2 is called available chlorine.

A good sample releases 35 – 38% available Cl_2. Theoretically the amount of Cl_2 in $CaOCl_2$ is 56%.

(ii)Autoxidation (Reaction in air)

On long standing in air, it decomposes

$6CaOCl_2 \rightarrow 5CaCl_2 + Ca(ClO_3)_2$

Because of this auto oxidation , it looses its available chlorine and bleaching property is affected.

(iii) Catalytic decomposition :

$2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2 + O_2$

Cobalt choride is the catalyst

(iv) A. With cold water : $CaOCl_2 \rightarrow Ca^{2+} + Cl^- + ClO^-$

B. with hot water : It undergoes auto oxidation giving Cl^- and ClO_3^- ; $3OCl^- \rightarrow ClO_3^- + 2Cl^-$.

(v) Oxidising property :

A. Lead salts $\rightarrow PbO_2$

B. $C_2H_5OH \xrightarrow[(O)]{CaOCl_2} CH_3CHO$

C. $C_2H_5OH \xrightarrow[(O)]{CaOCl_2} CHCl_3$

(d) Uses :

- Oxidsing agent, chlorinating agent
- Bleaching agent for cotton and paper pulp
- Disinfectant, germicide and sterilizes water. In the preparation of chloroform.

INTERHALOGEN COMPOUNDS

- The halogens react with each other forming binary compounds known as Interhalogen compounds. These are divided into four types . They are
  (i) AX (ii) AX_3 (iii) AX_5 (iv) AX_7
- These are all covalent compounds. In these compounds the atom 'A' exhibits the oxidation state +I, +III, V and +VII respectively.

SNO	Compounds	Ground / Excited electronic state	Hybridization undergone	Shape of the molecule
1	AX	ns^2np^5	-	Linear
2	AX_3	$ns^2np^4nd^1$	sp^3d	T-shape
3	AX_5	$ns^2np^3nd^2$	sp^3d	Square pyramid
4	AX_7	$ns^1np^3nd^3$	sp^3d^3	Pentagonal bipyramid