VII-A Group Elements (Subtopic-I)

General trends, hydrides, halides and Oxyacids of chlorine

- The elements, Fluorine (F), Chlorine (Cl), Bromine (Br) iodine (I), and Astatine (At) are VIIA group elements.
- **Electron configuration**
- Their general electron configuration in valence shell is $ns^2\ np^5$.
- The VIIA group elements except Astatine are called Halogens as their salts are found in sea water.
- Halogens react among themselves forming interhalogen compounds, which are more reactive than the halogen molecules.
- **Oxidation States**
- O.N. of F is always -1
- Oxidation states of other halogens = - 1, + 1, + 3, + 4, + 5, + 6, + 7
- **Physical state**
- Halogens exist as diatomic covalent molecules.
- The only type of attractions between Halogen molecules are vanderwaal's forces.
- The physical state of Halogens changes from gaseous to solid state due to increase in Van der waals forces. From fluorine (gas) to Iodine (solid) the density of the element increase with increase of atomic number of the Halogen (i.e. as atomic mass increases) with an increase in the density the Vander wall's force of attraction between molecules also proportionately increases consequently the physical state changes as follows.

  $F_2(gas), Cl_2(gas), Br_2(liquid), I_2(solid)$
- Iodine is the Halogen present in sea weeds.
- **Atomic radius order:** F < Cl < Br < I. This is due to

  1. Increase in the no. of shell and

  2. Increase of magnitude of screening effect.
- **Colour :** $F_2 =$ light yellow gas

  $Cl_2 =$ Greenish yellow gas

  $Br_2 =$ Reddish brown liquid

  $I_2 =$ Violet solid

- The colour of halogens is due to absorption of visible light by their molecules and thereby excitation of outer electron to higher energy level.
- **Ionisation potential**
- The lonisation potentials of halogens are very high.
- The Ionisation potentials decrease from Fluorine to Iodine, due to the increase in atomic size.
- **Electron affinity and electro negativity**
- Electron affinity values of halogens are very high.
- The electron affinity of fluorine is less than chlorine though it is most electronegative. This is due to its small size.
- Electron affinity values of Halogens are in Cl > F > Br > I.
- **Bond dissociation energy**
- Bond dissociation energies of Halogens are in the order $Cl_2 > Br_2 > F_2 > I_2$.
- **Oxidizing nature**
- Order of oxidizing power is $F > Cl > Br > I$.
- Stability order of aqueous halides $F^- > Cl^- > Br^- > I^-$.
- Reduction potentials order: $F_2 > Cl_2 > Br_2 > I_2$.
- Strong oxidizing power of F_2 is due to

  1) Low ΔH of dissociation of F – F bond

  2) High ΔH of hydration of F^-.
- **Chemical properties**
- Halogens are highly reactive elements they can react with metals as well as non-metal and other substances. The order of reactivity of Halogens is $F_2 >> Cl_2 > Br_2 > I_2$
- **Reaction with water**
- Chlorine reacts with water to form HCl and HOCl

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

- Chlorine water contains HCl and HOCl.
- Chlorine acts as a bleaching agent in the presence of water or moisture due to formation of HOCl.
- The bleaching action of chlorine in the presence of water or moisture is due to oxidation or liberation of nascent oxygen.

$$HOCl \rightarrow HCl + (O)$$

- I_2 neither reacts nor dissolves in water due to positive free energy change $(+\Delta G)$.

- **Reaction with hydrogen (hydrides)**
- The reactivity of Halogens with hydrogen decreases from $F_2 to I_2$.
- The stability of the hydrides decreases from HF to HI due to decrease in their dissociation energies.

  The stability order of hydrogen halides is HF > HCl > HBr > HI.
- **Reaction with NH_3**
- When excess chlorine reacts with ammonia to form an unstable Nitrogen trichloride and HCl.

  $3Cl_2 + NH_3 \rightarrow 3HCl + NCl_3$.
- Chlorine reacts with excess ammonia to give NH_4Cl liberating Nitrogen.

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

Reaction with alkalies

- Fluorine reacts with cold and dil. NaOH to form NaF, H_2O & O_2.

  $2F_2 + 4NaOH \rightarrow 4NaF + 2H_2O + O_2$
- Cl_2, Br_2 and I_2 react with cold and dil. NaOH to form halide and hypo halites. The oxidation number of halogen changes form 0 to -1 & + 1.

  $Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$

  $Br_2 + 2NaOH \rightarrow NaBr + NaOBr + H_2O$

  $I_2 + 2NaOH \rightarrow NaI + NaOI + H_2O$
- $CI_2 Br_2$ and I_2 react with hot and conc. NaOH to form halide and halates. The oxidation state of halogen changes fro 0 to -1 and + 5.

  $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

  $3Br_2 + 6NaOH \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

  $3I_2 + 6NaOH \rightarrow 5NaI + NaIO_3 + 3H_2O$

  Oxidising power
- Due to low heat of dissociation of F_2 molecule and high hydration energy of F^- ion, fluorine acts as strong oxidizing agent.
- Chlorine oxidises Bromides to Bromine and lodides to lodine.

  $Cl_2 + 2KBr \rightarrow 2KCl$

  $Cl_2 + 2KI \rightarrow I_2 + 2KCl$
- Bromine oxidises iodides to Iodine

  $Br_2 + 2KI \rightarrow I_2 + 2KBr$

Properties of Oxyacids

- Acid strength of oxyacids of halogens : $HOCl > HOBr > HOI$
- HOCl is unstable and easily decomposed

  $HOCl \rightarrow HCl + (O)$
- $HClO_3$ is colourless, pungent smelling liquid,
- Salt of $HClO_3$ is called chlorate, a stable salt O_2 on heating
- $HClO_4$ is colourless liquid.
- $HClO_4$ dimerises due to H-bonds.
- Salt of $HClO_4$ is perchlorate salt.
- Perchlorate salts are strong oxidizing agents.
- **Structures and bond properties**

Ion	Hybridisation Sate of Cl	Shape
ClO_2^-	sp^3	Angular (bond angle = 111^0)
ClO_3^-	sp^3	Pyramidal (bond angle = 106^0)
ClO_4^-	sp^3	Tetrahedral (bond angle = 109.4^0)

- The order of Cl – O bond length $ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$
- The order of Cl – O bond energy $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$
- From $ClO^- to ClO_4^-$ ions, there is increase of no. of $\pi -$bonds and hence there is increase of delocalized $\pi -$bonded electrons.

VIIA GROUP ELEMENTS (SUBTOPIC-II)

Flourine, Chlorine, Bleaching power, Interhalogen compounds.

Flourne

- In Moissan method electrodes and electrolytic cell is made with Pt – Ir alloy.
- The products of electrolysis of fused KHF_2 are hydrogen at cathode and fluorine at anode.
- Fluorine forms XeF_2, XeF_4 and XeF_6 with xenon.
- In its hydride it forms hydrogen bonding and forms HF_2^- ion but of other halogens hydrides do not show hydrogen bonding.
- Fluorine is oxidising agent.

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

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

- HF is used for etching or marking glass. Fluoro Chloro Carbon is called Freon. It is used as a refrigerant.
- **Chlorine**
- Because it forms CuF_2 with fluorine. CuF_2 layer protects the metal form further attack of fluorine.
- Chlorine can be prepared by the oxidation of HCl with MnO_2

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

- In Nelson's cell method Chlorine is manufactured by the electrolysis brine or an aqueous solution of sodium chloride.
- In Nelson's cell, a perforated steel vessel acts as cathode and graphite rod acts as anode.
- $COCl_2$ is called phosgene. It is poisonous gas.
- $CCl_2.NO_2$ is called tear gas.
- $Cl - C_2H_4 - S - C_2H_4 - Cl$ Or $\left(C_2H_4Cl\right)_2$ S is called Mustard gas. It is used as war gas.
- Dichloro diphenyl trichloro ethane is known as DDT. It is a fungicide.

Bleaching powder

- Bleaching Powder is also called chloride of lime.
- The chemical name of Bleaching Powder is calcium chloro hypo chlorite.
- The oxidation states of chlorine in Bleaching Powder are -1 and +1.
- Bleaching Powder is unstable. On long standing it decomposes to from $CaCl_2$ and $Ca(ClO_3)_2$

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

- The hot aqueous solution of Bleaching Powder contains Ca^{2+}, Cl^- and ClO_3^- ions.
- A good sample of Bleaching Powder contains 35 - 35% of available chlorine.
- Percentage of Chlorine in bleaching powder is 56% [Theoriti cally]

Interhalogen compounds

- Inter halogen compounds are covalent and diamagnetic ClF is gas and the rest are solids or liquids at 298 K. Being polar inter halogen compounds are more reactive then halogens except fluorine.

All interhalogen compounds undergo hydrolysis giving halide ion.

$$BrF_5 + 3H_2O \rightarrow 5HF + HBrO_3$$