p-Block Elements (Halogen & Noble Gases)

Section (A_I) : Elements: Occurence & Isolation

Introduction :

The five representative elements fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are members of Group 17. These are collectively known as the **halogens** (Greek halo means salt and genes means born i.e., salt producers). The halogens are highly reactive non-metallic elements. Like Groups 1 and 2, the elements of Group 17 show great similarity amongst themselves. That much similarity is not found in the elements of other groups of the periodic table.

GROUP 17 ELEMENTS : THE HALOGENS FAMILY

Occurrence :

All halogens are very reactive & do not occurs in free state.

Element	Abundance	Source
F	544 ppm (13th most abundant element)	♦ Main Source : Fluorspar (CaF_2) or Fluorite ♦ Another Source : Fluoroapatite [$3Ca_3(PO_4)_2.CaF_2$] (Mainly source of P) Cryolite : Na_3AlF_6
Cl	126 ppm (20th most abundant element)	♦ Most abundant compound of Cl : NaCl (Sea water) Carnalite : $KCl.MgCl_2.6H_2O$.
Br	2.5 ppm	♦ Bromides occurs in sea water & brine lakes
I	0.46 ppm	♦ Iodides occurs in low conc. in sea water. ♦ Better source : Natural brines ♦ Impurities ($NaIO_3$ & $NaIO_4$) in Chile salt petre ($NaNO_3$)
At	Radioactive & has a short half-life ($t_{1/2}$ = 7.2 Hr.)	♦ Do not occur in nature

Allotropy :

All the elements of halogen family generally do not show allotropy.

Atomicity :

All halogens exist as diatomic (X_2) molecule.

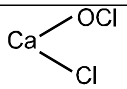
Element Preparation

Fluorine

S.No.	Method	Process	Comments
1.	Moisson's Method (Electrolytic)	$CaF_2 + \underset{(Conc.)}{H_2SO_4} \rightarrow CaSO_4 + 2HF$	
		$KF + HF \rightarrow K[HF_2]$	♦ $K[HF_2] \Leftrightarrow K^+[F–H–F]^-$
		Fluorine cell : Electrodes : Anode : Carbon Cathode : Steel Electrolyte : KHF_2 (1 part) + HF (5 part) Temperature of the both : –24ºC **Reaction :** $K[HF_2] \longrightarrow KF + HF$ $KF \longrightarrow K^+ + F^-$ **On electrolysis :** At cathode : $K^+ + e^- \rightarrow K$ $K + HF \rightarrow KF + H$ $2H \rightarrow H_2(g)$ At Anode : $F^- \rightarrow F + e^-$ $2F \rightarrow F_2$	♦ Anhydrous HF is only slightly ionized & is therefore a poor conductor of electricity. Thus a mixture of KF & HF in 1 : 13 mole ratio is electrolysed to increase the conductivity. **Difficulties:** ♦ HF is corrosive & also very toxic ♦ H_2O should not be present. Otherwise F_2 will oxidize H_2O to O_2 $2F_2 + 2H_2O \rightarrow 4HF + O_2$ ♦ Graphite anodes must not be used, since graphite reacts with fluorine, forming a polymeric substance known as graphite fluoride.
		Modern method : Electrolyte : KF : HF = 1 : 2 Temperature : 72ºC	
		Note : It is not possible to prepare fluorine by electrolysis of aqueous solution of NaF or KF. It is because when aqueous solution of KF is subjected to electrolysis, there will be following two oxidation in competition at anode, $H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e^-$ SOP = – 1.23 V and $F^- \longrightarrow 1/2F_2 + e^-$ SOP = – 2.87 V As a matter of rule that substance will be oxidise whose SOP is higher therefore water gets oxidise at anode and not F^-.	
2.	Chemical Method	$2KMnO_4 + 2KF + 10HF + 3H_2O_2 \rightarrow$ $2K_2MnF_6 + 8H_2O + 3O_2$ $K_2[MnF_6] + 2\,SbF_5 \longrightarrow 2K\,[SbF_6] + MnF_3 + F_2$ $\left\{\begin{array}{l} \text{via} \\ MnF_4 \longrightarrow MnF_3 + \frac{1}{2}F_2 \end{array}\right\}$	♦ The stronger Lewis acid SbF_5 displaces the weaker one, MnF_4 from its salt. ♦ MnF_4 is unstable and readily decomposes to give MnF_3 and fluorine.

Chlorine

S.No.	Method	Process	Comments
1.	Laboratory Preparation	$H_2SO_4 + NaCl \rightarrow HCl + NaHSO_4$ $4HCl + MnO_2 \rightarrow MnO_2 + 2H_2O + Cl_2\uparrow$	♦ HCl is purified first passed through H_2O then through conc. H_2SO_4 to remove H_2O further dried by CaO & P_4O_{10}
2.	Commercially:		
(i)	By electrolysis of aq. NaCl solution in the manufacture of NaOH	$2NaCl + 2H_2O \xrightarrow{\text{Electrolyte}} 2NaOH + Cl_2 + 2H_2$ $2NaCl \xrightarrow{\text{Electrolyte}} 2Na + Cl_2$	

(ii)	Deacon's process	$4HCl + O_2 \underset{440^oC}{\overset{CuCl_2\ Catalyst}{\rightleftharpoons}} 2Cl_2 + 2H_2O + \Delta$	♦ Air is used to oxidize HCl instead MnO_2 ♦ Reaction is reversible ♦ Conversion 65%
(iii)	Electrolysis of Brine	**Reactions:** At Anode : $2Cl^- \rightarrow Cl_2 + 2e^-$ At cathode : $Na^+ + e^- \rightarrow Na$ $2Na + 2H_2O \rightarrow 2NaOH + H_2$ Side reactions may also occur if the products mix: $2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$ $2OH^- + Cl_2 \rightarrow 2OCl^- + H_2$ (Hypochlorite) At anode (small extent reaction) : $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	
3.	Miscellaneous Reactions	**(a)** $[NaCl+HNO_3 \rightarrow NaNO_3+HCl] \times 3$ $HNO_3+3HCl \rightarrow NOCl+Cl_2+2H_2O$ $3NaCl+4HNO_3 \rightarrow 3NaNO_3+NOCl+Cl_2+ 2H_2O$ (nitrosyl chloride) $2NOCl+O_2 \rightarrow 2NO_2+Cl_2$ $NO_2+H_2O \rightarrow HNO_3$ (to be recycled)	♦ These methods are exclusively used only for chlorine.
		(b)  $Ca(OCl)Cl$ + 2HCl → $CaCl_2 + Cl_2 + H_2O$	
		(c) $2KMnO_4+16HCl \rightarrow 2KCl+2MnCl_2+5Cl_2+8H_2O$	
		(d) $PbO_2 + 4\ HCl \rightarrow PbCl_2, + Cl_2 + 2\ H_2O$	
		(e) When Cl_2 is used for the chlorination of hydrocarbon, the by-product is HCl. The HCl is catalytically oxidised into H_2O & Cl_2 using copper powder mixed with rare earth chlorides. $4\ HCl + O_2 \xrightarrow{Cu\ powder\ +\ rare\ earth\ chloride} 2H_2O + 2Cl_2$	

Bromine:

S.No.	Method	Process
1.	Extracted from sea water	♦ Cl_2 gas passed through solution to oxidize Br^- to Br_2 $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$ ↓ Removed by steam of air & passed to solution of Na_2CO_3. **Reactions :** $3Br_2 + 3Na_2CO_3 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$ $5NaBr + NaBrO_3 + 2H_2SO_4 \rightarrow 5HBr + HBrO_3 + 3Na_2SO_4$ $5HBr + HBrO_3 \rightarrow 3Br_2 + 3H_2O$ ↓ Pure Bromine
2.	Common method	$2\ NaBr + 3H_2SO_4 + MnO_2 \xrightarrow{\Delta} Br_2 + MnSO_4 + 2NaHSO_4 + 2H_2O$ (conc.)

Iodine:

S.No.	Method	Process	Comments
1.	Source : Chile saltpetre	♦ Pure $NaNO_3$ is obtained by dissolving salt petre in H_2O & crystallizing $NaNO_3$ ♦ Iodate residues thus accumulated & concentrate in mother liquor ♦ Concentrate → divided into 2 part 1st part reduced with $NaHSO_3$ $2IO_3^- + 6HSO_3^- \rightarrow 2I^- + 6SO_4^{2-} + OH^-$ 2nd part is mixed $3I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$	♦ Chile salt petre is mainly $NaNO_3$ ♦ Contain traces of $NaIO_3$ (Sodium iodate) & $NaIO_4$ (Sodium periodate) ♦ Purified by sublimation
2.	Source: Natural blue	$2I^- + Cl_2 \rightarrow I_2 + 2Cl^-$ $\downarrow$ blown out by air	
3.	From sea-weeds:	$2NaI + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + I_2 + 2H_2O$	♦ Liberated iodine is condensed in series of earthen ware known as aludels.
4.	Other Method	$CuSO_4 + 2KI \rightarrow K_2SO_4 + CuI_2$ $2CuI_2 \rightarrow Cu_2I_2 + I_2$	♦ This I_2 gets dissolved into KI forming KI_3, since I_3^- ions are yellow, therefore solution develops yellow colour.

Section (B_I+ C_I + D_I) : Periodic Trends, Properties of Elements and Chemical Bonding

Atomic & Physical Properties :

S.No.	Property	F	Cl	Br	I
1.	Atomic Number	9	17	35	53
2.	Atomic Mass/g mol^{-1}	19	35.45	79.90	126.90
3.	Electronic configuration *General electronic configuration=($ns^2\ np^5$)*	[He] $2s^22p^5$	[Ne] $3s^23p^5$	[Ar] $3d^{10}4s^24p^5$	[Kr] $4d^{10}5s^2\ 5p^5$
4.	Covalent Radius / pm *(F < Cl < Br <I)*	64	99	114	133
5.	Ionic Radius X^- / pm *(F < Cl < Br <I)*	133	184	196	220
6.	Ionization enthalpy / (kJ mol^{-1}) *(F > Cl > Br > I)*	1680	1256	1142	1008
		♦ *Due to increase in atomic size, ionisation enthalpy decreases down the group.*			
7.	Electron gain enthalpy /(kJ mol^{-1}) *(Cl > F > Br > I)*	– 333	– 349	– 325	– 296
		♦ *Maximum negative electron gain enthalpy in the corresponding period.* ♦ *Negative electron gain enthalpy of* ***fluorine < chlorine****: Due to small size of fluorine atom. As a result, there are strong inter-electronic repulsions in the relatively small 2p orbitals of fluorine and thus, the extra electron (incoming) does not experience much attraction.*			
8.	Distance X -X/pm *(F_2 < Cl_2 < Br_2 < I_2)*	143	199	229	266
9.	Enthalpy of dissociation (X_2)/kJ mol^{-1} *(Cl – Cl > Br – Br > F – F > I –I)*	158.8	242.6	192.8	151.1
		♦ *Smaller enthalpy of dissociation of F_2 is due to relatively larger electron-electron repulsion among the lone pairs in F_2 molecule.*			
10.	Electronegativity *(F > Cl > Br > I)*	4	3.2	3.0	2.7
11.	Melting point / K *(F < Cl < Br < I)*	54.4	172	265.8	386.6

12.	Boiling point / K *($F < Cl < Br < I$)* *(State at room temp.)*	84.9 Gas	239.0 Gas	332.5 Liquid	458.2 Solid
13.	$\Delta_{Hyd}H$ (X^-) / kJ mol^{-1} *($F > Cl > Br > I$)*	515 ♦ *Smaller the ion, higher is the hydration energy.*	381	347	305
14.	$E^{\ominus}$ / V (SRP) ; $X_2(g) + 2e^- \rightarrow 2X^-(aq)$ *($F_2 > Cl_2 > Br_2 > I_2$)* *(Order of oxidising power)*	2.87 ♦ *More the value of the SRP, more powerful is the oxidising agent.*	1.36	1.09	0.54
15.	Colour (at room temp.)	Pale green yellow gas.	Greenish-yellow gas	Reddish brown liquid	Dark violet solid
16.	Oxidization state	–1	–1, +1, +3, +5, +7	–1, +1, +3, +5, +7	–1, +1, +3, +5, +7

CHEMICAL PROPERTIES :

Oxidation states and trends in chemical reactivity

(1) All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states also.

(2) The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms e.g., in interhalogens, oxides and oxoacids.

(3) The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only –1 oxidation state.

(4) All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

(5) The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase.

(6) The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials.

(7) Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids.

(8) The reactions of iodine with water is non- spontaneous I^- can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.

$$2F_2(g) + 2H_2O(\ell) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(\ell) \longrightarrow HX(aq) + HOX(aq) \text{ ; (where X = Cl or Br)}$$

$$4I^-(aq) + 4H^+(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(\ell)$$

Standard Reduction Potential (SRP)

$X_2 + 2e^- \longrightarrow 2X^-$

$F_2 + 2e^- \longrightarrow 2F^-$ $E° = +2.87$ V ; $Cl_2 + 2e^- \longrightarrow 2Cl^-$ $E° = +1.36$ V

$Br_2 + 2e^- \longrightarrow 2Br^-$ $E° = +1.09$ V ; $I_2 + 2e^- \longrightarrow 2I^-$ $E° = +0.54$ V

More the value of the SRP, more powerful is the oxidising agent. Hence the order of oxidising power is $F_2 > Cl_2 > Br_2 > I_2$

Since SRP is the highest for F_2 (among all elements of periodic table), it is a strongest oxidising agent.

Hydration energy of X^-

Smaller the ion, higher is the hydration energy.

Halide ion	F^-	Cl^-	Br^-	I^-
Hydration energy (in kJ/mol)	515	381	347	305

Anomalous behaviour of fluorine

(1) The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F–F bond dissociation enthalpy, and non availability of d orbitals in valence shell.

(2) Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements).

(3) It forms only one oxoacid while other halogens form a number of oxoacids.

(4) Hydrogen fluoride is liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

Reactivity towards oxygen :

Oxidation State	F	Cl	Br	I
–1	OF_2, O_2F_2	–	–	–
+1		Cl_2O	Br_2O	
+4		Cl_2O	BrO_2	I_2O_4
+5		–	–	I_2O_5
+6		Cl_2O_6, ClO_3	–	
+7		Cl_2O_7		I_2O_7

(1) Halogens form many oxides with oxygen but most of them are unstable.

(2) Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is the thermally stable at 298 K.

(3) These oxide are essentially oxygen fluorides because of the higher electronegativity of flurorine than oxygen. Both are strong fluorinating agents.

(4) O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

(5) Chlorine, bromine and iodine form oxides in which the oxidation states of these halogen vary from + 1 to + 7.

(6) A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br. The higher oxides of halogens tend to be more stable than the lower ones.

(7) Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

(8) The bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides and exist only at low temperature. They are very powerful oxidising agents.

(9) The iodine oxides, I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is very good oxidising agent and is used in the estimation of carbon monoxide.

S.No.	Reaction with Elements	General Reaction	Comments
1.	H_2	$X_2 + H_2 \rightarrow 2HX$ → $F_2 + H_2 \rightarrow 2HF$ → $Cl_2 + H_2 \rightarrow 2HCl$ → $Br_2 + H_2 \rightarrow 2HBr$ → $I_2 + H_2 \rightarrow 2HI$	♦ All the halogens ♦ Reactivity towards H_2 decrease down the group. ♦ $F_2 \rightarrow$ Violently react ♦ $I_2 \rightarrow$ Slow at room temp.
		The acidic strength of these acids increases in the order : HF < HCl < HBr < HI. The stability of these halides decreases down the group due to decrease in bond (H–X) dissociation enthalpy in the order : H – F > H – Cl > H –Br > H – I	
2.	Metal	$nX_2 + 2M \rightarrow 2MX_n$ → $2Na + Cl_2 \rightarrow 2NaCl$ → $2Al + 3Cl_2 \rightarrow 2AlCl_3$ → $2Fe + 3Cl_2 \rightarrow 2FeCl_3$ → $Mg_{(s)} + Br_{2(\ell)} \rightarrow MgBr_{2(s)}$ → $2Ag + F_2 \rightarrow 2AgF$	♦ Most metals form halides ♦ F the most vigorous The ionic character of halides is MF > MCl > MBr > MI.
3.	P	$\underset{\text{(Limited)}}{3X_2} + 2P \rightarrow PX_3$ → $P_4 + 6Cl_2 \rightarrow 4PCl_3$ → $P_4 + 6Br_2 \rightarrow 4PBr_3$ → $P_4 + 6I_2 \rightarrow 4PI_3$ $\underset{\text{(Excess)}}{5X_2} + 2P \rightarrow PX_5$ $\left[2P + 5Cl_2 \rightarrow 2PCl_5\right]$	♦ All the halogens form trihalides As, Sb, Bi — Also form trihalides ♦ F, Cl & Br form pentahalides AsF_5, SbF_5, BiF_5, $SbCl_5$
4.	S	$\underset{\text{(Limited)}}{X_2} + 2S \rightarrow S_2X_2$ $\left[S_8 + 4Cl_2 \rightarrow 4S_2Cl_2\right]$ $\underset{\text{(exess)}}{2Cl_2} + S \rightarrow SCl_4$ $3F_2 + S \rightarrow SF_6$	♦ Cl and Br ♦ Cl only ♦ F only

5.	O_2	$O_2 + F_2 \xrightarrow[\text{silent electric discharge}]{\text{only in presence of}} O_2F_2$	
6.	Other non-metals	$C + 2F_2 \rightarrow CF_4$ $2B + 3F_2 \rightarrow 2BF_3$	♦ Wood, charcoal, phosphorous, arsenic, antimony, boron, silicon react with F_2 producing a flame.
7.	Other Halogens	$X_2 + X'_2 \rightarrow 2XX'$ $X_2 + X'X \rightarrow XX'_3$	♦ Halogens combine amongst themselves to form a number of compounds known as interhalogen of the types XX', XX'_3, XX'_5 and XX'_7 where X is a larger size halogen and X' is smaller size halogen.

S.No.	**Reaction with Compounds**	**General Reaction**	**Comments**
1.	H_2O	$2F_2 + 2H_2O \rightarrow 4HF + O_2$	♦ Vigorous reaction with F.
		$X_2(g) + H_2O(\ell) \rightarrow HX(aq.) + HOX(aq.)$ X = Cl or Br	♦ Cl > Br > I (F not at all)
		$4I^-(aq.) + 4H^+(aq.) + O_2 \rightarrow 2I_2(s) + 2H_2O(\ell)$	♦ I reaction in reverse direction
2.	Base		
(i)	NH_3	For F_2 $2NH_3 + 3F_2 \rightarrow N_2 + 6HF$	♦ It is the distinction from other halogens.
		For Cl_2 and Br_2 *NH_3 Excess* $3X_2 + 8NH_3 \rightarrow N_2 + 6NH_4X$ $[3Cl_2 + 8NH_3 \rightarrow N_2 + 6NH_4Cl]$ *X_2 Excess* $NH_3 + 3X_2 \rightarrow NX_3 + 3HX$ $[NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl]$	♦ NX_3 is explosive
		For I_2 $NH_3(g) + I_2 \rightarrow$ No Reaction $\underset{\text{(Ammonia liquor)}}{NH_3(aq) + I_2(s)} \xrightarrow[\text{A slurry is formed which can be dried and on hammering it explodes causing sound (crakers)}]{} \underbrace{NI_3 . NH_3}_{\text{an explosive (Nitrogentriiodide ammoniated)}} + 3HI$ $8NI_3.NH_3 \rightarrow 5N_2 + 9I_2 + 6NH_4I$	
(ii)	NaOH	For F_2 $2F_2 + \underset{\text{(dilute)}}{2NaOH} \rightarrow OF_2(g) + 2NaF + H_2$ $2F_2 + \underset{\text{(concentrated)}}{4NaOH} \rightarrow O_2(g) + 4NaF + 2H_2O$	♦ Dilute alkali forms oxygen difluoride & with concentrated alkali liberates O_2**.**
		For Cl_2, Br_2, I_2 $\underset{\text{(Cold \& dil.)}}{2NaOH} + Cl_2 \rightarrow NaCl + NaOCl + H_2O$ $\underset{\text{(hot \& conc.)}}{6NaOH} + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$	♦ These reactions are also given by Br_2 and I_2.
(iii)	$Ca(OH)_2$ (Dry slaked lime)	$2Ca(OH)_2 + 2Cl_2 \rightarrow \underset{\text{(Bleaching powder)}}{Ca(OCl)_2} + CaCl_2 + 2H_2O$	♦ Composition of bleaching powder $= Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$
3.	Acid	Generally no reaction is shown with acids.	
4.	H_2S	For F_2 $H_2S + 4F_2 \rightarrow SF_6 + 2HF$	

		For Cl_2, Br_2, I_2 $X_2 + H_2S \rightarrow 2HX + S$ $\left[Cl_2 + H_2S \rightarrow 2HCl + S\right]$	♦ Cl_2, Br_2 & I_2 oxidize S^{2-} to S ♦ It show Cl has great affinity for hydrogen to form HCl
5.	SO_2	$X_2 + SO_2 \rightarrow SO_2X_2$ $\left[SO_2 + Cl_2 \rightarrow SO_2Cl_2\right]$	♦ F & Cl
6.	CO	$X_2 + CO \rightarrow COX_2$ $\left[CO + Cl_2 \rightarrow COCl_2\right]$	♦ Cl and Br form carbonyl halides

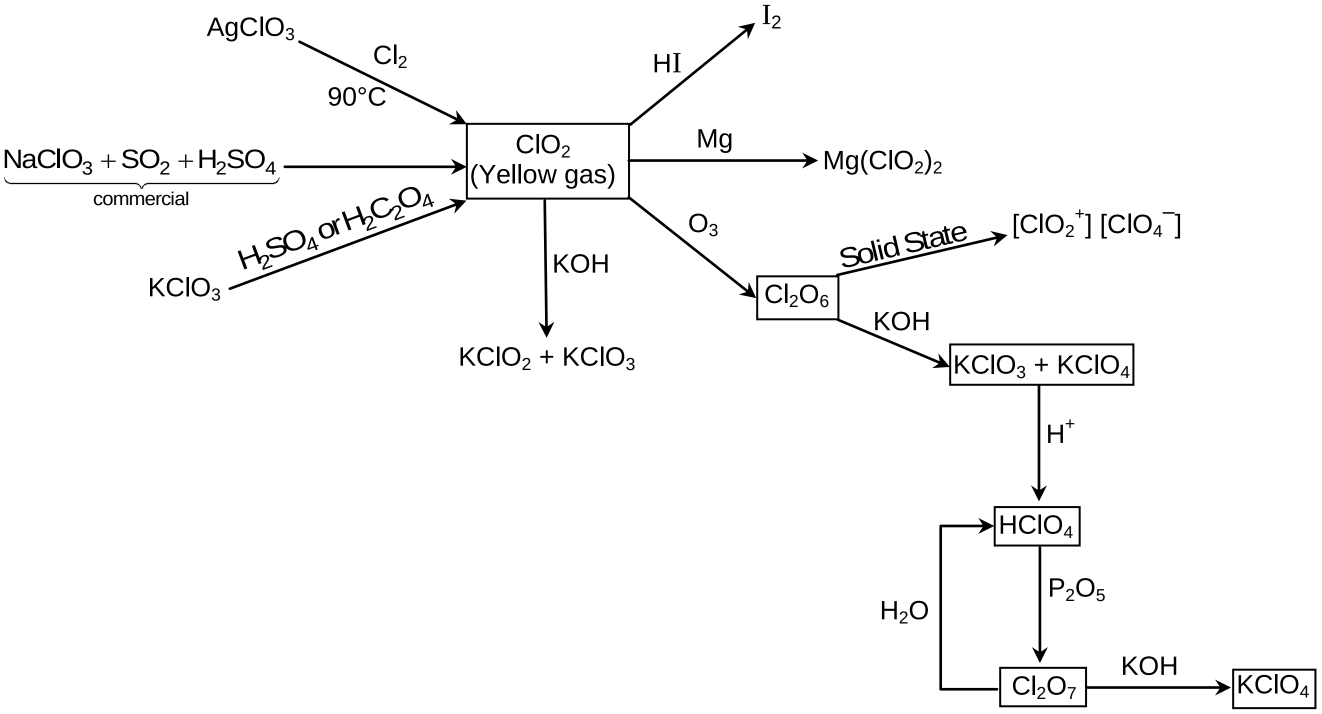
Other Reactions			
For F_2			
1.	Reaction with SO_3	$2SO_3 + F_2 \xrightarrow[AgF]{180^oC} FSO_2\,OOSO_2F$	
2.	Reaction with SiO_2	$SiO_2\,(s) + 2F_2\,(g) \rightarrow SiF_4\,(g) + O_2\,(g)$	♦ It attacks glass at about 100^0C. ♦ The reaction is slow with dry F_2.
3.	Oxidising character	$F_2 + 2NaX \rightarrow 2NaF + X_2$; where (X= Cl, Br, I) (a) It can oxidise all other halide ions into halogen molecules (b) It can oxidise ClO_3^- into ClO_4^- and IO_3^- to IO_4^- $F_2 + ClO_3^- + H_2O \rightarrow 2F^- + ClO_4^- + 2H^+$ (c) It can oxidise HSO_4^- into $S_2O_8^{2-}$ $2HSO_4^- + F_2 \rightarrow 2F^- + S_2O_8^{2-} + 2H^+$	♦ It is the most powerful oxidising agent.
For Cl_2			
	Oxidising and bleaching properties	*Chlorine dissolves in water giving HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.*	
		$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$ $Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$ $SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$ $I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$ $X^- + Cl_2 \rightarrow X_2 + 2Cl^-$	♦ Oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid. ♦ Chlorine oxidises both Br^- and I^- to Br_2 and I_2 respectively.
	Bleaching action	$Cl_2 + H_2O \rightarrow 2HCl + O$ Bleaching action of SO_2 $SO_2 + 2H_2O \rightarrow H_2\,SO_4 + 2H$ $SO_3^{2-} + \underset{\text{material}}{\text{Coloured}} \rightarrow SO_4^{2-} + \underset{\text{Colourless material}}{\text{Reduced}}$	♦ It is a powerful bleaching agent ♦ bleaching action is due to oxidation. ♦ Coloured substance + O → Colourless substance ♦ It bleaches vegetable or organic matter in the presence of moisture. ♦ Bleaching effect of chlorine is permanent. ♦ The bleaching action of SO_2 is temporary because it takes place through reduction. ♦ $\underset{\text{Colourless material}}{\text{Reduced}} \xrightarrow{O_2 \text{ of air}} \underset{\text{material}}{\text{Coloured}}$
For Br_2			
		$(Br_2.8H_2O) \longleftarrow$ Clathrate compound	♦ Reddish brown liquid, fairly soluble in water. It also forms hydrate like Cl_2

For I_2			
1.	Reaction with Hypo	$S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ (thiosulphate ions) (tetrathionate ions)	♦ This reaction is the basis of iodometric titration, which is carried out for the estimation of iodine using starch indicator.
2.	Reaction with $KClO_3$ or $KBrO_3$	$2KClO_3 + I_2 \xrightarrow{\Delta} 2KIO_3 + Cl_2$; $2KBrO_3 + I_2 \xrightarrow{\Delta} 2KIO_3 + Br_2$	

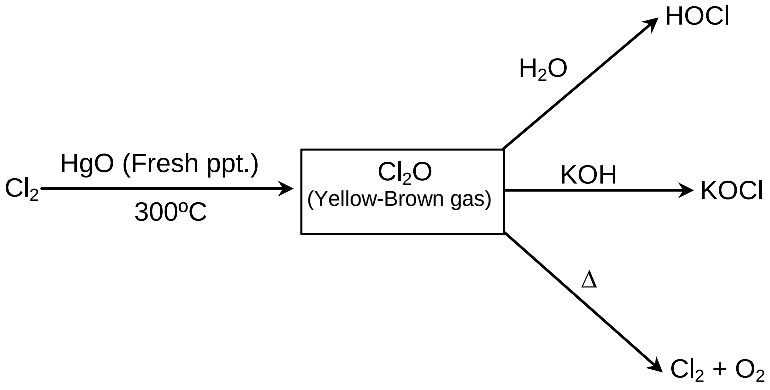
Section (E_I) : Oxides, Hydroxides & Oxyacids

OXIDES OF CHLORINE

CHLORINE DIOXIDE (ClO_2) :



Dichlorine Monoxide (Cl_2O) :



OXY-ACIDS OF HALOGENS

HOX SERIES :

HYPO-FLOROUS ACID [HOF] :

HOF has been prepared by trapping F_2 and H_2O in unreactive matrix of solid N_2 at very low temperature and photolysing the gases.

$$F_2 + H_2O \xrightarrow{hv} HOF + HF$$

Recent method is by passing, F_2 over ice at 0ºC and removing the product into a cold trap.

$$H_2O + F_2 \xrightleftharpoons{-40^\circ C} HOF + HF$$

- HOCl, HOBr and HOI are not very stable and are known only in aqueous solution.

HYPO-CHLOROUS ACID [HClO] :

PREPARATION :

(i) The acid is known only in solution, It is obtained by shaking precipitate of HgO with chlorine water.

$$2HgO + 2Cl_2 + H_2O \longrightarrow Hg_2OCl_2 \text{ (Oxychloride of mercury)} + 2HClO$$

(ii) Commercially, it is obtained by passing CO_2 through suspension of bleaching powder and then distilling.

$$2CaOCl_2 + H_2O + CO_2 \longrightarrow CaCl_2 + CaCO_3 + 2HClO$$

Maximum concentration obtained is 25% as in the process of distillation, the acid decomposes into its anhydrides, Cl_2O.

$$2HOCl \longrightarrow H_2O + Cl_2O$$

PROPERTIES :

(i) It is a weak acid. Its concentrated solution is yellow in colour while dilute solution is colourless. It is unstable and decomposes.

$$2HClO \longrightarrow 2HCl + O_2$$

(ii) It dissolves magnesium with evolution of hydrogen.

$$Mg + 2HClO \longrightarrow Mg(ClO)_2 + H_2$$

(iii) With alkalies, it forms salts called hypochlorites.

(iv) It acts as a powerful oxidising and bleaching agent. This is due to release of nascent oxygen easily.

$$HClO \longrightarrow HCl + O$$

HXO_2 SERIES :

CHLOROUS ACID [$HClO_2$] :

PREPARATION :

It is obtained in aqueous solution when barium chlorite suspension in water is treated with H_2SO_4. The insoluble barium sulphate is filtered off.

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_2$$

PROPERTIES:

(i) The freshly prepared solution is colourless but it soon decomposes to ClO_2 which makes the solution yellow.

$$5\ HClO_2 \longrightarrow 4\ ClO_2 + HCl + 2H_2O$$

(ii) Salts of $HClO_2$ are called chlorite and prepared by one of the following methods.

$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

$$2ClO_2 + Na_2O_2 \longrightarrow 2NaClO_2 + O_2$$

Chlorites are used as bleaching agents. They are stable in alkaline solution even when boiled, but in acid solution they disproportionate, particularly when heated.

$$5HClO_2 \longrightarrow 4ClO_2 + HCl + 2H_2O \quad \text{and} \quad 4HClO_2 \longrightarrow 2ClO_2 + HClO_3 + HCl + H_2O$$

(iii) The acid liberates iodine from KI.

$$4KI + HClO_2 + 2H_2O \longrightarrow 4KOH + HCl + 2I_2$$

HXO_3 SERIES

CHLORIC ACID [$HClO_3$] :

PREPARATION :

This acid is only known in solution. The acid is prepared by the action of the dilute H_2SO_4 on barium chlorate.

$$Ba\ (ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2HClO_3.$$

After reaction, $BaSO_4$ is removed by filtration, and the filtrate is evaporated in vacuum till 40 percent solution is obtained. However, further concentration by evaporation leads to decomposition.

$$3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$$

$HBrO_3$ can be prepared by similar method using $Ba(BrO_3)_2$.

PROPERTIES :

(i) Concentrated acid is colourless and pungent smelling liquid. It decomposes in light. However, it is stable in dark.

(ii) It acts as a strong oxidising and bleaching agent in light.

(iii) Organic substances like paper, cotton, wool, etc., catch fire in contact with the acid.

(iv) $HClO_3$ oxidises SO_2 to SO_3 : $HClO_3 + 3SO_2 \longrightarrow HCl + 3SO_3$

(v) $HClO_3$ when evaporates to dryness decomposes giving ClO_2.

$$4HClO_3 \longrightarrow 4ClO_2(g) + 2H_2O(g) + O_2(g)$$

(vi) $HBrO_3$ is not very stable, but is known in solution, and as salts.

(vii) HIO_3 is formed by oxidation of I_2 with concentrated HNO_3 or O_3.

$$8H^+ + 10NO_3^- + I_2 \longrightarrow 2IO_3^- + 10NO_2 + 4H_2O$$

(viii) IO_3^- oxidises I^- to I_2 : $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

(ix) Iodic acid is reasonably stable and exists as a white solid.

(x) $2KClO_3 \xrightarrow[MnO_2]{150°C} 2KCl + 3O_2$

(xi) $4KClO_3 \xrightarrow{\text{low temperature}} 3KClO_4 + KCl$ (in absence of catalyst)

(xii) $2Zn(ClO_3)_2 \xrightarrow{\Delta} 2ZnO + 2Cl_2 + 5O_2$

(xiii) Chlorates are used in fire work.

HXO_4 SERIES

PERCHLORIC ACID [$HClO_4$] :

PREPARATION:

(i) It is the most stable oxy-acid of chlorine. Anhydrous $HClO_4$ is obtained by doing distillation of $KClO_4$ (potassium perchlorate), with 96-97.5% H_2SO_4 under low pressure at 90-160°C.

$$KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$$

(ii) An aqueous solution of the acid is obtained by reacting barium perchlorate with calculated quantity of dilute H_2SO_4. The insoluble barium sulphate is removed by filtration.

$$Ba(ClO_4)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_4$$

(iii) $NaClO_3 + H_2O \xrightarrow{\text{Electrolysis}} ClO_4^- + 2H^+ + 2e^-$

(iv) $NH_4ClO_4 + HNO_3 \longrightarrow HClO_4 + NH_4NO_3$

(v) $4ClO_3^- \xrightarrow{\Delta} 3ClO_4^- + Cl^-$

(vi) $HClO_4.2H_2O + 2H_2S_2O_7 \longrightarrow HClO_4$ (obtained as anhydrous $HClO_4$) $+ 2H_2SO_4$

PROPERTIES:

(i) Anhydrous $HClO_4$ is a colourless liquid which turns dark on keeping. It fumes in moist air.

(ii) It is one of the strongest acid and ionises as follows :

$$HClO_4 \longrightarrow H^+ + ClO_4^-$$

(iii) It dissolves most of the metals.

$$Zn + 2HClO_4 \longrightarrow Zn(ClO_4)_2 + H_2$$

(iv) Hot concentrated acid (73%) behaves as a remarkable oxidising agent :

$$4HClO_4 \longrightarrow 2Cl_2 + 7O_2 + 2H_2O$$

(v) $2HClO_4 + P_2O_5 \longrightarrow 2HPO_3 + Cl_2O_7$

❍ $Mg(ClO_4)_2$ is used in dry batteries and is also an effective desiccant called **anhydrone**. $KClO_4$ is used in fire works and flares.

Some important orders :

(a) Acidic strength :

(i) $HI > HBr > HCl > HF$ (ii) $HOCl > HOBr > HOI$ (iii) $HClO_4 > HClO_3 > HClO_2 > HClO$

(b) Oxidising powder

(i) $F_2 > Cl_2 > Br_2 > I_2$

(ii) $BrO_4^- > IO_4^- > ClO_4^-$ (According to electrode potential)

(c) Order of disproportionations

$3XO^- \longrightarrow 2X^- + XO_3^-$ (hypohalite ion) ; $IO^- > BrO^- > ClO^-$

Section (FI) :

HALOGEN ACIDS (HCl, HBr & HI)

- Pure anhydrous HX compounds refer as hydrogen halides.
- Their aqueous solutions as hydrohalic acids.

Preparation :

(1) By direct combination of elements :

$H_2 + Cl_2 \longrightarrow 2HCl$; $H_2 + Br_2 \xrightarrow{Pt} 2HBr$; $H_2 + I_2 \xrightarrow{Pt,\,450^\circ C} 2HI$

(2) By heating a halide with concentrated acid :

(a) $NaCl + H_2SO_4 \xrightarrow{150^\circ C} NaHSO_4 + HCl$

$NaHSO_4 + NaCl \xrightarrow{550^\circ C} Na_2SO_4 + HCl$

This method is called as salt cake method as it involves the formation of $NaHSO_4$ (salt cake). HCl cannot be dried over P_2O_5 (P_4O_{10}) or quick lime since they react with gas chemically.

$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

$P_4O_{10} + 3HCl \longrightarrow POCl_3 + 3HPO_3$

HCl is, hence dried by passing through concentrated H_2SO_4.

(b) HBr (or HI) cannot be prepared by heating bromide (iodide) with concentrated H_2SO_4 because HBr and HI are strong reducing agents and reduce H_2SO_4 to SO_2 and get themselves oxidised to bromine and iodine respectively.

$KX + H_2SO_4 \longrightarrow KHSO_4 + HX$

$H_2SO_4 + 2HX \longrightarrow SO_2 + X_2 + 2H_2O$ (X = Br or I)

Hence, HBr and HI are prepared by heating bromides and iodides respectively with concentrated H_3PO_4.

$3KBr(KI) + H_3PO_4 \longrightarrow K_3PO_4 + 3HBr\ (HI)$

(3) By reaction of P_4 (Laboratory Method) :

$P_4 + 6Br_2\ (6I_2) \longrightarrow 4PBr_3\ (4PI_3)$

$PBr_3\ (PI_3) + 3H_2O \longrightarrow 3HBr\ (HI) + H_3PO_3$

(4) By passing H_2S / SO_2 into solutions of halogens :

$H_2S + X_2 \longrightarrow 2HX + S$

$SO_2 + 2H_2O + X_2 \longrightarrow 2HX + H_2SO_4$

(5) PROPERTIES :

(i) These are colourless, pungent smelling gases with acidic tastes.

(ii) These are neither combustible nor supporter of combustion.

(iii) When perfectly dry, they have no action on litmus, but in presence of moisture, they turn blue litmus red, showing acidic nature. Among HX, HI is the strongest and HF is the weakest acid.

(iv) These are quite soluble in water.

HCl ionises as below : $HCl(g) + H_2O(\ell) \longrightarrow H_3O^+\ (aq) + Cl^-\ (aq)$; $K_a = 10^7$

It's aqueous solution is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water.

(v) When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$Au + 4\,H^+ + NO_3^- + 4\,Cl^- \longrightarrow [AuCl_4]^- + NO + 2\,H_2O$

$3\,Pt + 16\,H^+ + 4\,NO_3^- + 18\,Cl^- \longrightarrow 3\,[PtCl_6]^{2-} + 4\,NO + 8\,H_2O$

(6) Reducing property and stability of hydracids :

HCl : It is quite stable and hence is oxidised by strong oxidising agents like MnO_2, $KMnO_4$, $K_2Cr_2O_7$, PbO_2, Pb_3O_4.

(i) $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

(ii) $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

(iii) $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

(iv) $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$;

(v) $Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$

Therefore, HCl is a weak reducing agent.

HBr : It is not very stable and hence more easily oxidised or acts as a strong reducing agents.

(i) In addition to above reducing properties of HCl, it also reduces H_2SO_4 to SO_2 which is not done by HCl.

$$H_2SO_4 + HBr \longrightarrow SO_2 + Br_2 + 2H_2O$$

(ii) Aqueous HBr on exposure to atmospheric oxygen is oxidised to bromine (yellow)

$$4HBr + O_2 \longrightarrow 2\,Br_2 + 2H_2O$$

HI : It is least stable hydrogen halide. It is readily oxidised and thus acts as a powerful reducing agent. In addition to reaction shown by HCl, it shows following reactions also.

(i) $H_2SO_4 + 2HI \longrightarrow SO_2 + I_2 + H_2O$
$H_2SO_4 + 6HI \longrightarrow S + 3I_2 + 4H_2O$
$H_2SO_4 + 8HI \longrightarrow H_2S + 4I_2 + 4H_2O$

(ii) $2HNO_3 + 2HI \longrightarrow 2NO_2 + I_2 + 2H_2O$

(iii) $2HNO_2 + 2HI \longrightarrow 2NO + I_2 + 2H_2O$

(iv) $HIO_3 + 5HI \longrightarrow 3I_2 + 2H_2O$

(v) $K_2S_2O_8 + 2HI \longrightarrow K_2SO_4 + I_2 + H_2SO_4$

(vi) $2FeCl_3 + 2HI \longrightarrow 2FeCl_2 + I_2 + 2HCl$

(vii) Aqueous solution of acid, if exposed to O_2 is oxidised to iodine.

$$4HI + O_2 \longrightarrow 2I_2 + 2H_2O$$

(7) Detection of cation:

HCl : $AgNO_3 + HCl \longrightarrow AgCl\downarrow$ (white) $+ HNO_3$
$(CH_3COO)_2Pb + 2HCl \longrightarrow PbCl_2\downarrow$ (white) $+ 2CH_3COOH$
$Hg(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2\downarrow$ (white) $+ 2HNO_3$

HBr : $AgNO_3 + HBr \longrightarrow AgBr\downarrow$ (pale yellow) $+ HNO_3$
$(CH_3COO)_2Pb + 2HBr \longrightarrow PbBr_2\downarrow$ (white) $+ 2CH_3COOH$

HI : $AgNO_3 + HI \longrightarrow AgI\downarrow$ (bright yellow) $+ HNO_3$
$(CH_3COO)_2Pb + 2HI \longrightarrow PbI_2\downarrow$ (yellow) $+ 2CH_3COOH$
$HgCl_2 + 2HI \longrightarrow HgI_2\downarrow$ (scarlet red) $+ 2HCl$

HI reacts with $CuSO_4$ liberating iodine via the formation of cupric iodide (not by HCl or HBr).

$$2CuSO_4 + 4HI \longrightarrow 2CuI_2 + 2H_2SO_4\ ; \quad 2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

USES :

(i) HCl is used in preparation of Cl_2, chlorides, aqua regia, glucose (from corn starch), medicines, laboratory as reagents, cleaning metal surfaces before soldering or electroplating. It is also used for extracting glue from bones and purifying bone black.

(ii) HBr is used as laboratory reagent for preparing bromo derivatives like sodium bromides and potassium bromide.

(iii) HI is used as reducing agent in organic chemistry.

HYDROFLUORIC ACID [H_2F_2, HF] :

PREPARATION :

H_2 and F_2 combine with each other very violently (even in dark) to form HF. So simple reaction cannot be used for its preparation, special methods are employed for its preparation.

(1) Laboratory Method : Anhydrous HF is obtained by heating dry potassium hydrogen fluoride in a copper retort connected with copper condenser.

$$KHF_2 \xrightarrow{\Delta} KF + HF$$

(2) Industrial Method : HF is prepared by heating fluorspar (CaF_2) with concentrated H_2SO_4.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

(3) Aqueous HF being corrosive to glass, is stored in wax lined bottles or vessel made of copper or monel. In glass or silica bottles, it attacks them as follows:

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O\ ; \quad CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O\ ;\ SiF_4 + 2HF \longrightarrow H_2SiF_6$$

This action of HF on silica (silicates) is used for etching glass. The glass surface to be etched is coated with wax, the design, is scratched on glass through wax coating and this is then treated with 40% solution.

PROPERTIES :

(i) It is colourless, corrosive liquid with pungent smell with high boiling point due to hydrogen bonding.

(ii) Dry HF does not attack metals under ordinary conditions (except K), but in presence of water it dissolves metals with liberation of hydrogen gas.

(iii) It is a weak dibasic acid (due to strong HF bond) and forms two series of salt.

$$NaOH + H_2F_2 \longrightarrow NaHF_2 + H_2O \;;\; NaHF_2 + NaOH \longrightarrow 2NaF + H_2O$$

(iv) HF also react reacts with CCl_4 to form freons.

$$CCl_4 + HF \longrightarrow CFCl_3 + HCl \quad ; \quad CFCl_3 + HF \longrightarrow CF_2Cl_2 + HCl.$$

Section (H_I) : Other compounds (Inter halogens, Bleaching powder, Pseudo halides & Poly halides)

BLEACHING POWDER :

Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.

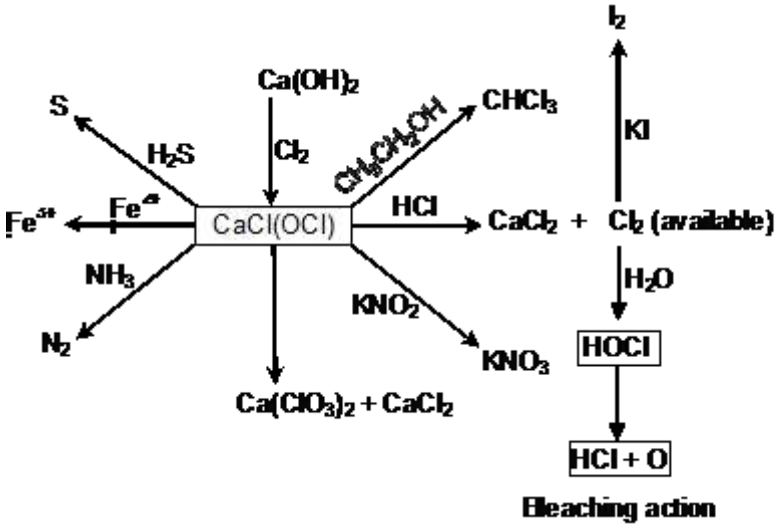
The composition of bleaching powder is $Ca(OCl)_2 . CaCl_2 . Ca(OH)_2 . 2H_2O$.

PREPARATION:

$$Ca(OH)_2 + Cl_2 \xrightarrow{40^\circ C} Ca(OCl)Cl + H_2O$$

Properties

It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.



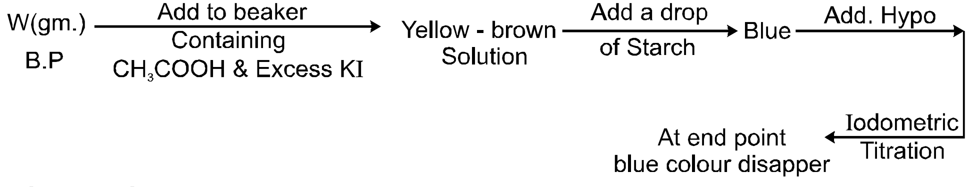
ESTIMATION OF AVAILABLE CHLORINE :

Let the weight of sample of bleaching powder be W g.

Add into a beaker containing acetic acid solution and excess KI. A yellow brown solution is formed (I_3^-)

$$I_2 + I^- \longrightarrow I_3^-$$

Now few drops of starch solution is added into it. An intensive blue color is observed. Now hypo is used as the titrant. Note the volume where the blue colour disappear.



Reaction involved :

$$CaOCl_2 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + H_2O + Cl_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$$

Calculation : $\%Cl = \dfrac{[M_{hypo} \times V_{hypo}] \times \frac{1}{2} \times 71}{W} \times 100$

INTERHALOGEN COMPOUNDS :

We know that halogen atoms have different electronegativity. Due to this difference in electronegativity the halogen atoms combine with each other and give rise to the formation of binary covalent compounds, which are called interhalogen compounds. These are of four types XX', XX'_3, XX'_5 and XX'_7 where X is a larger size halogen and X' is smaller size halogen.

Some Properties of Interhalogen Compounds

Type	Formula	Physical state and colour	Structure
XX'_1	ClF BrF IF^a $BrCl^b$ ICl IBr	Colourless gas pale brown gas detected spectroscopically gas ruby red solid (α-form) brown red solid (β-form) black solid	– – – – – –
XX'_3	ClF_3 BrF_3 IF_3 ICl_3	colourless gas yellow green liquid yellow powder orange solid	Bent T- shaped Bent T- shaped Bent T- shaped Bent T- shaped
XX'_5	IF_5 BrF_5 ClF_5	colourless gas but solid below 77 K colourless liquid colourless liquid	Square pyramidal Square pyramidal Square pyramidal
XX'_7	IF_7	colourless gas	Pentagonal bipyramidal

PREPARATION :

(i) By the direct combination of halogens :

$Cl_2 + F_2 \text{ (equal volumes)} \xrightarrow{473\text{ K}} 2ClF$; $Cl_2 + 3F_2 \text{ (excess)} \xrightarrow{573\text{ K}} 2ClF_3$;

$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl$;

(ii) Diluted with water : $Br_2\text{ (g)} + 3F_2 \longrightarrow 2BrF_3$

(iii) F_2 is diluted with N_2 : $I_2 + 3F_2 \xrightarrow{-78^\circ C} 2IF_3$

(iv) F_2 is taken in freon : $Br_2 + 5F_2 \text{ (excess)} \longrightarrow 2BrF_5$

(v) IF_7 can not be prepared by direct combination of I_2 & F_2.

(vi) From lower interhalogens :

$ClF + F_2 \longrightarrow ClF_3$; $ClF_3 + F_2 \text{ (excess)} \xrightarrow{350^\circ C} ClF_5$

$BrF_3 + F_2 \text{ (excess)} \xrightarrow{200^\circ C} BrF_5$; $IF_5 + F_2 \xrightarrow{270^\circ C} IF_7$

This method is generally applied for the preparation of halogen fluorides.

(vii) Other methods :

$6HCl + KIO_3 + 2KI \longrightarrow 2KCl + 3H_2O + 3ICl$

$Cl_2 + ClF_3 \xrightarrow{250-350^\circ C} 3ClF$; $KCl + 3F_2 \xrightarrow{200^\circ C} KF + ClF_5$

$3I_2 + 5AgF \longrightarrow 5AgI + IF_5$; $8F_2 + PbI_2 \longrightarrow PbF_2 + 2IF_7$

PROPERTIES :

(i) These compounds may be gases, liquids or solids.
Gases : ClF, BrF, ClF_3 , IF_7 ; Liquids : BrF_3, BrF_5 ; Solids : ICl, IBr, IF_3, ICl_3.

(ii) Interhalogens containing fluorine are colourless but inter halogens consisting of heavier halogens are coloured. The intensity of colour increases with increase in the molecular weight of the compounds.

(iii) All interhalogens are covalent molecules and are diamagnetic in nature since all the valence electrons present as bonding or non-bonding electrons are paired.

(iv) The boiling points increases with the increase in the electronegativity difference between A and B atoms.

(v) Thermal stability of AB type interhalogen compounds decreases with the decrease in electronegativity difference between A and B atoms. IF > BrF > ClF > ICl > IBr > BrCl.

More polar is the A–B bond more is the stability of interhalogen.

(vi) Interhalogen compounds are more reactive than the parent halogens but less reactive than F_2.

$ICl + 2Na \longrightarrow NaI + NaCl$

The order of reactivity of some interhalogens is as follows :

$ClF_3 > BrF_3 > IF_7 > BrF_5 > BrF$.

(vii) **Hydrolysis** : All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when AB), halite (when AB_3), halate (when AB_5), and perhalate (when AB_7) anion derived from the larger halogen.

$AB + H_2O \longrightarrow HB + HOA$

$BrCl + H_2O \longrightarrow HCl + HOBr$; $ICl + H_2O \longrightarrow HCl + HIO$

$ICl_3 + 2H_2O \longrightarrow 3HCl + HIO_2$; $IF_5 + 3H_2O \longrightarrow 5HF + HIO_3$

$IF_7 + 6H_2O \longrightarrow 7HF + H_5IO_6$; $BrF_5 + 3H_2O \longrightarrow 5HF + HBrO_3$

Oxidation state of A atom does not change during hydrolysis.

(viii) Reaction with non-metallic and metallic oxides :

$4BrF_3 + 3SiO_2 \longrightarrow 3SiF_4 + 2Br_2 + 3O_2$; $4BrF_3 + 2WO_3 \longrightarrow 2WF_6 + 2Br_2 + 3O_2$

(x) Reaction with alkali metal halides :

$IBr + NaBr \longrightarrow NaIBr_2$; $ICl_3 + KCl \longrightarrow KICl_4$

USES :

These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U .

$U(s) + 3\ ClF_3(l) \longrightarrow UF_6\ (g) + 3\ ClF\ (g)$

Pseudohalogens and Pseudohalides :

(i) A few ions are known, consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. They are therefore called pseudohalide ions.

(ii) Pseudohalide ions are univalent, and these form salts resembling the halide salts. For example, the sodium salts are soluble in water, but the silver salts are insoluble.

(iii) The hydrogen compounds are acids like the halogen acid HX. Some of the pseudohalide ions combine to form dimers comparable with the halogen molecule X_2. These include cyanogens $(CN)_2$, thiocyanogen $(SCN)_2$ and selenocyanogen $(SeCN)_2$.

Anion		Acid		Dimer	
CN^-	Cyanide ion	HCN	Hydrogen cyanide	$(CN)_2$	Cyanogen
SCN^-	Thiocyanate ion	HSCN	Thiocyanic acid	$(SCN)_2$	Thiocyanogen
$SeCN^-$	Selenocyanate ion	HOCN	Cyanic acid	$(SeCN)_2$	Selenocyanogen
OCN^-	Cyanate ion	H_2NCN	Cyanamide		
NCN^{2-}	Cyanamide ion	HN_3	Hydrogen azide		
N_3^-	Azide ion				

The best known pseudohalide is CN^-. This resembles Cl^-, Br^- and I^- in the following respects.

(a) It forms an acid HCN.

(b) It can be oxidized to form a molecule cyanogen $(CN)_2$.

(c) It forms insoluble salts with Ag^+, Pb^{2+} and Hg^+

(d) Interpseudohalogen compounds ClCN, BrCN and ICN can be formed.

(e) AgCN is insoluble in water but soluble in ammonia, as is AgCl.

(f) It forms a large number of complexes similar to halide complexes.

e.g. $[Cu(CN)_4]^{2-}$ and $[CuCl_4]^{2-}$ and $[Co(CN)_6]^{3-}$ and $[CoCl_6]^{3-}$

GROUP 18 ELEMENTS : (THE NOBLE GASES / ZERO GROUP FAMILY)

Group 18 consists of six elements: helium, neon, argon, krypton, xenon and radon. All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed as noble gases.

Section (A_{II}) : Elements: Occurence & Isolation

(i) All the noble gases except radon occur in the atmosphere.

(ii) Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite.

(iii) The main commercial source of helium is natural gas.

(iv) Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of ^{226}Ra.

$$^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

(v) Most abundant element in air is Ar. Order of abundance in the air is Ar > Ne > Kr > He > Xe.

Section (B_{II} + C_{II} + D_{II}) : Periodic Trends, Properties of Elements and Chemical Bonding

(1) Electronic Configuration :

All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$. Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

(2) Ionisation Enthalpy :

Due to stable electronic configuration these gases exhibit very high ionisation enthalpy. However, it decreases down the group with increases in atomic size.

(3) Atomic Radii :

Atomic radii increase down the group with increase in atomic number.

(4) Electron Gain Enthalpy :

Since noble gases have stable electronic configurations, they have no tendency to accept the electron and therefore, have larger positive values of electron gain enthalpy.

(5) Physical properties :

(i) All the noble gases are mono-atomic.

(ii) They are colourless, and tasteless.

(iii) They are sparingly soluble in water.

(iv) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.

(v) Helium has the lowest boiling point (4.2K) of any known substance. It has a unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Table : Atomic and physical properties

Element	He	Ne	Ar	Kr	Xe
Atomic Number	2	10	18	36	54
Atomic Mass	4	20.18	39.10	83.80	131.30
Electronic configuration	$1s^2$	[He] $2s^2$ $2p^6$	[Ne] $3s^2$ $3p^6$	[Ar] $3d^{10}4s^2$ $4p^6$	[Kr] $4d^{10}5s^2$ $5p^6$
Atomic Radius (pm)	120	160	190	200	220
Ionization enthalpy / (kJ mol^{-1})	2372	2080	1520	1351	1170
Density (at STP)/g cm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}
Melting point / K	–	24.6	83.8	115.9	161.3
Boiling point / K	4.2	27.1	87.2	119.7	165.0

(6) Chemical Properties :

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2 np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

(iii) In March 1962, Neil Bartlett, prepared a red compound which is formulated as $O_2^+ PtF_6^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol^{-1}) was almost identical with that xenon (1170 kJ mol^{-1}).

(iv) He also prepared same type of compound with $Xe^+ PtF_6^-$ by mixing Pt F_6 and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

(v) The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail.

(vi) Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique.

(vii) No true compounds of Ar, Ne or He are yet known.

(viii) If Helium is compressed and liquified it forms He(I) liquid at 4.2 K. This liquid is a normal liquid like any other liquid. But if it is further cooled then He(II) is obtained at 2.2 K, which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity.

(7) Clatherate compounds :

(i) Inert gas molecules get trapped in the cages formed by the crystal structure of water.

(ii) During the formation of ice Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clatherate compounds.

(iii) In this compounds there are no chemical bonds. They do not possess an exact chemical formula but approx it is 6 water molecules : 1 inert gas molecule.

(iv) The cavity size is just smaller than the atom of the noble gas. Such compounds are also formed by the other organic liquids like dihydroxybenzene (for example quinol).

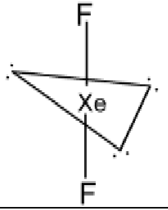
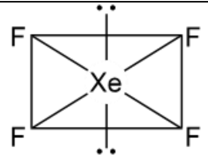
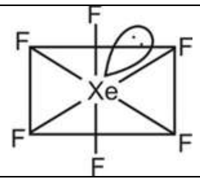
(v) The smaller noble gases He and Ne do not form clathrate compounds because the gas atoms are small enough to escape from the cavities.

(vi) Clathrate provides a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.

Section (G_{II}) : Compounds of Xenon

Halides & Oxyhalides :

(I) XENON FLUORIDES :

Compounds	Structures	Hybridisation	Geometry	Shape
XeF_2		sp^3d	trigonal bipyramidal	linear
XeF_4		sp^3d^2	octahedral	square planar
XeF_6		sp^3d^3	pentagonal bipyramidal	distorted octahedron

PREPARATION :

Xenon reacts directly with fluorine when the gases are heated at 300-600°C in a sealed nickel vessel and the products formed depend on the Xe / F_2 ratio.

$$Xe + F_2 \longrightarrow 2 : 1 \text{ mixture} \xrightarrow{400°C,\ 1\ atm} XeF_2$$

$$Xe + F_2 \longrightarrow 1 : 5 \text{ mixture} \xrightarrow{600°C,\ 7\ atm} XeF_4$$

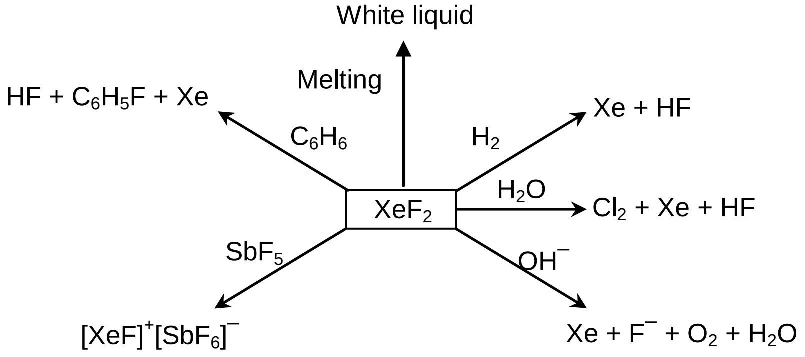
$$Xe + F_2 \longrightarrow 1 : 20 \text{ mixture} \xrightarrow{600°C,\ 7\ atm} XeF_6$$

PROPERTIES :

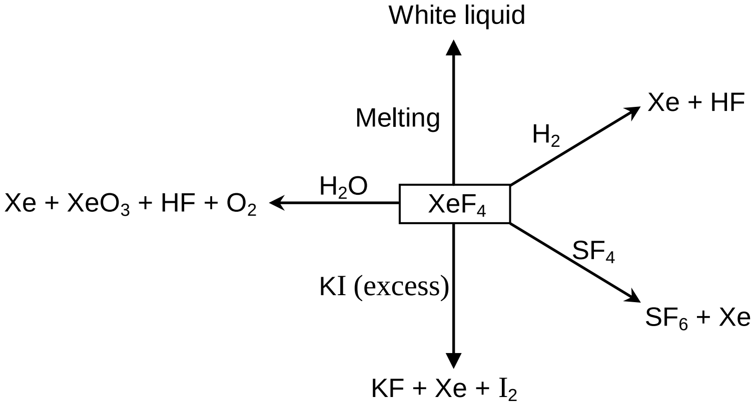
These are colourless (white) solids. They can be sublimed at room temperature and can be stored indefinitely in nickel or monel (an alloy of nickel) containers.

Chemical properties:

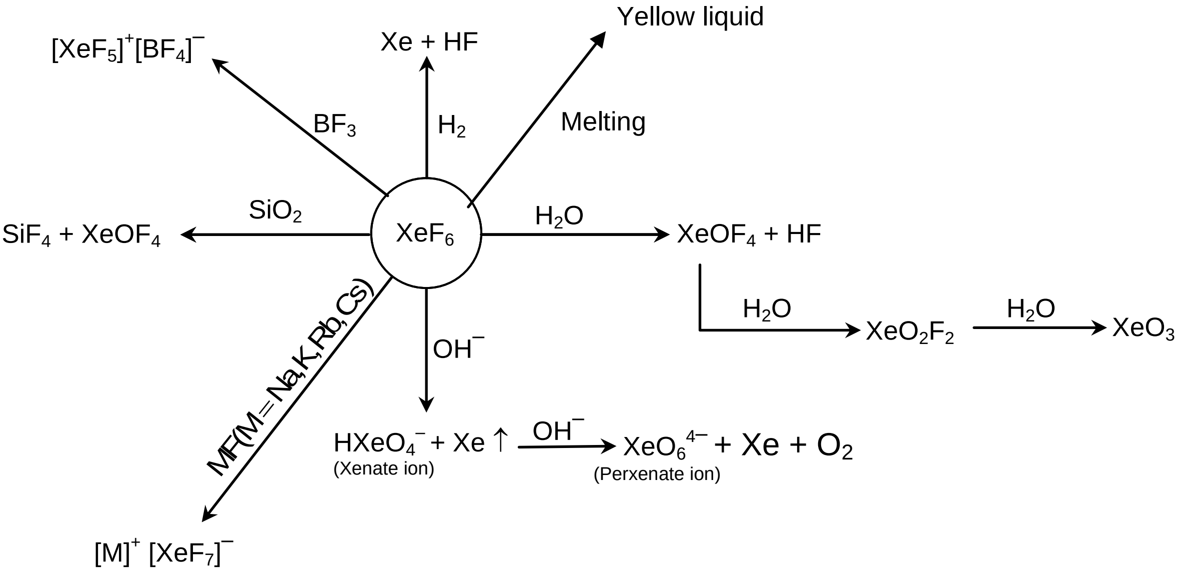
1. **XeF_2 :**



2. **XeF_4 :**



3. **XeF_6**



(II) XENON–OXYGEN COMPOUNDS :

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$6\ XeF_4 + 12\ H_2O \longrightarrow 4\ Xe + 2\ XeO_3 + 24\ HF + 3\ O_2$

$XeF_6 + 3\ H_2O \longrightarrow XeO_3 + 6\ HF$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$XeF_6 + H_2O \longrightarrow XeOF_4 + 2\ HF$

$XeF_6 + 2\ H_2O \longrightarrow XeO_2F_2 + 4\ HF$

XeO_3 is a colourless explosive solid and has a pyramidal molecular structure. $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.

USES :

(i) Helium is a non–inflammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas–cooled nuclear reactors.

(ii) Liquid helium (b.p.4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures.

(iii) Helium is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis.

(iv) Helium is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

(v) Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

(vi) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.

(vii) Argon is also used in the laboratory for handling substances that are air–sensitive.

(viii) Xenon and Krypton are used in light bulbs designed for special purposes.