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CHEMISTRY

Target : JEE (Main)

**p-BLOCK ELEMENTS
(HALOGEN & NOBLE GASES)**

p-BLOCK ELEMENTS (HALOGEN & NOBLE GASES)

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JEE (MAIN) SYLLABUS

Group - 17 : Preparation, properties and uses of chlorine and hydrochloric acid; Trends in the acidic nature of hydrogen halides; Structures of Interhalogen compounds and oxides and oxoacids of halogens.
Group - 18 : Occurrence and uses of noble gases; Structures of fluorides and oxides of xenon.

JEE(ADVANCED) SYLLABUS

Isolation/preparation and properties of the following non-metals : Halogens Preparation and properties of the following compounds :
Halogens: Hydrohalic acids, oxides and oxyacids of chlorine, bleaching powder; Xenon fluorides.

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p-Block Elements (Halogens Family and Noble Gases)

Introduction :

Group 13 to 18 of the periodic table of elements constitute the p-block. The p-block contains metals, metalloids as well as non-metals. The p-block elements have general valence shell electronic configuration $ns^2 np^{1-6}$. The first member of each group from 13-17 of the p-block elements differ in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d-orbitals. The first member of a group also has greater ability to form $p\pi-p\pi$ multiple bonds to itself (e.g. $C=C$, $C\equiv C$, $N\equiv N$) and to element of second row (e.g. $C=O$, $C=N$, $C\equiv N$, $N=O$) compared to the other members of the same group. The highest oxidation of p-block element is equal to the group number minus 10. Moving down the group, the oxidation state two less than the highest group oxidation state becomes more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding)

Group 17 Elements : The Halogen Family

Occurrence :

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

Element	Abundance	Source
F	544 ppm (13 th most abundant element)	<ul style="list-style-type: none"> Main Source : Fluorspar (CaF_2) or Fluorite Another Source : Fluoroapatite [$3Ca_3(PO_4)_2 \cdot CaF_2$] (Mainly source of P)
Cl	126 ppm (20 th most abundant element)	<ul style="list-style-type: none"> Most abundant compound of Cl : NaCl
Br	2.5 ppm	<ul style="list-style-type: none"> Bromides occurs in sea water & brine lakes
I	0.46 ppm	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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.

p-Block Elements (Halogen & Noble Gases)
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 ² 2p ⁵	[Ne] 3s ² 3p ⁵	[Ar] 3d ¹⁰ 4s ² 4p 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 electrons-electrons 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.	Δ _{Hyd} H (X ⁻) / kJ mol ⁻¹ (F > Cl > Br > I)	515	381	347	305
		♦ Smaller the ion, higher is the hydration energy.			
14.	E ⁰ / V (SRP) ; X ₂ (g) + 2e ⁻ → 2X ⁻ (aq) (F ₂ > Cl ₂ > Br ₂ > I ₂) (Order of oxidising power)	2.87	1.36	1.09	0.54
		♦ More the value of the SRP, more powerful is the oxidising agent.			
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

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MAIN PHN - 2

p-Block Elements (Halogen & Noble Gases)

Chemical Properties

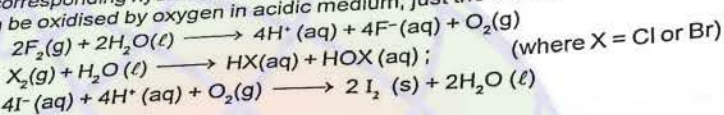
Oxidation states and trends in chemical reactivity

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

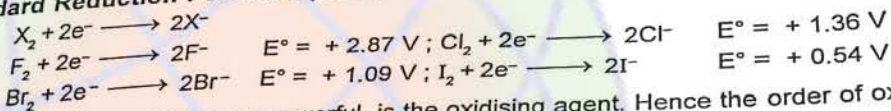
The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only -1 oxidation state.

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.

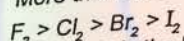
The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F₂ is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. 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.



Standard Reduction Potential (SRP)



More the value of the SRP, more powerful is the oxidising agent. Hence the order of oxidising power is



Since SRP is the highest for F₂ (among all elements of periodic table), it is a strongest oxidising agent.

Hydration energy of X⁻

Smaller the ion, higher is the hydration energy.

F ⁻	Cl ⁻	Br ⁻	I ⁻	
515	381	347	305	in kJ/mol

Anomalous behaviour of fluorine

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. Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogens form a number of oxoacids. Hydrogen fluoride is liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

- (i) **Reactivity towards hydrogen** : They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine with increasing atomic number. They dissolve in water to form hydrohalic acids. 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.

- (ii) **Reactivity towards oxygen** : Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF₂ and O₂F₂. However, only OF₂ is the thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O₂F₂ oxidises plutonium to PuF₆ and the reaction is used in removing plutonium as PuF₆ from spent nuclear fuel.

Chlorine, bromine and iodine form oxides in which the oxidation states of these halogen vary from +1 to +7. 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. Chlorine oxides, Cl₂O, ClO₂, Cl₂O₆ and Cl₂O₇ are highly reactive oxidising agents and tend to explode. ClO₂ is used as a bleaching agent for paper pulp and textiles and in water treatment. The bromine oxides, Br₂O, BrO₂, BrO₃ are the least stable halogen oxides and exist only at low temperature.



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MAIN PHN - 3

p-Block Elements (Halogen & Noble Gases)

They are very powerful oxidising agents, 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.

- (iii) **Reactivity towards metals** : Halogen react with metals to form metal halides. For e.g., bromine reacts with magnesium to give magnesium bromide.
- (iv) **Reactivity of halogen towards other halogens** : Halogens combine amongst themselves to form a number of compounds known as interhalogen of the types AB , AB_2 , AB_3 and AB_4 , where A is a larger size halogen and B is smaller size halogen.

Solved Examples

- Ex.1** Although electron gain enthalpy of fluorine is less negative as compared to chloride, fluorine is a stronger oxidising agent than chlorine. Why?
Sol. It is due to : (i) low enthalpy of dissociation of F-F bond, (ii) high hydration enthalpy of F^- .
- Ex.2** Covalent radius of fluorine is 64 pm but the bond length is not equal to 128 pm and that is 143 pm and bond energy is found to be comparable to I_2 .
Sol. This may be attributed to $\ell.p - \ell.p$ repulsions due to small size of F atom.
- Ex.3** Why are halogens strong oxidising agents ?
Ans. (i) They have low bond dissociation energy, (ii) They have high electron affinity.
- Ex.4** Fluorine exhibits only -1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation states also. Explain.
Sol. Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have d orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

CHLORINE (Cl_2) :

Preparation :

S.No.	Method	Process	Comments
1.	Laboratory Preparation	$H_2SO_4 + NaCl \rightarrow HCl + NaHSO_4$ $4HCl + MnO_2 \rightarrow MnO_2 + 2H_2O + Cl_2 \uparrow$	<ul style="list-style-type: none"> • 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	$4HCl + O_2 \xrightleftharpoons[440^\circ C]{CuCl_2 \text{ Catalyst}} 2Cl_2 + 2H_2O + \Delta$	<ul style="list-style-type: none"> • Air is used to oxidize HCl instead MnO_2 • Reaction is reversible • Conversion 65%
(iii)	Electrolysis of Brine	<p>Reactions: At Anode : $2Cl^- \rightarrow Cl_2 + 2e^-$ At cathode : $Na^+ + e^- \rightarrow Na$</p> <hr/> <p>$2Na + 2H_2O \rightarrow 2NaOH + H_2$</p> <p>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)</p> <p>At anode (small extent reaction) : $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$</p>	

p-Block Elements (Halogen & Noble Gases)

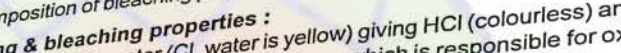
Properties :

- (i) It is a greenish-yellow gas with pungent and suffocating odour. It is about 2-5 times heavier than air. It can be liquefied into greenish-yellow liquid which boils at 239 K. It is soluble in water.
- (ii) At low temperature it forms a hydrate with water having formula $Cl_2 \cdot 8H_2O$ which is infact a clathrate compound.
- (iii) **Reaction with metals :**
 $2Al + 3Cl_2 \rightarrow 2AlCl_3$; $2Fe + 3Cl_2 \rightarrow 2FeCl_3$
- Reaction with non-metals :**
 $P_4 + 6Cl_2 \rightarrow 4PCl_3$; $S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$
- (iv) **Affinity for hydrogen :** It reacts with compounds containing hydrogen and form HCl.
 $H_2 + Cl_2 \rightarrow 2HCl$; $H_2S + Cl_2 \rightarrow 2HCl + S$

Reaction with NaOH :

- (a) $2NaOH$ (cold & dilute) + $Cl_2 \rightarrow NaCl + NaClO + H_2O$
- (b) $6NaOH$ (hot & concentrated) + $3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

Reaction with dry slaked lime, $Ca(OH)_2$: To give bleaching powder.

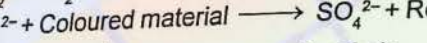
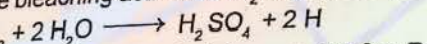
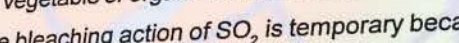
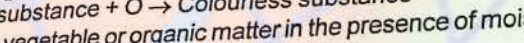


The composition of bleaching powder is $Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O$

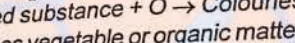
Oxidising & bleaching properties :

Chlorine dissolves in water (Cl_2 water is yellow) giving HCl (colourless) and HOCl (colourless). Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

- (a) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

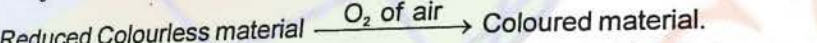
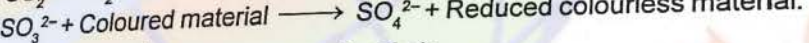


- (b) It is a powerful bleaching agent ; bleaching action is due to oxidation.



Coloured substance + O → Colourless substance
 It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.

Note : The bleaching action of SO_2 is temporary because it takes place through reduction.



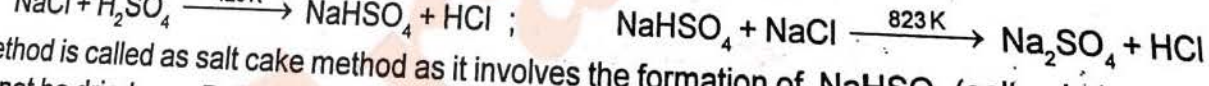
Uses : Cl_2 is used

1. for bleaching wood pulp (required for the manufacture of paper and rayon), bleaching cotton and textiles,
2. in the manufacture of dyes, drugs and organic compounds such as CCl_4 , $CHCl_3$, DDT, refrigerants, etc.
3. in the extraction of gold and platinum.
4. in sterilising drinking water and
5. preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($CICH_2CH_2SCH_2CH_2Cl$).

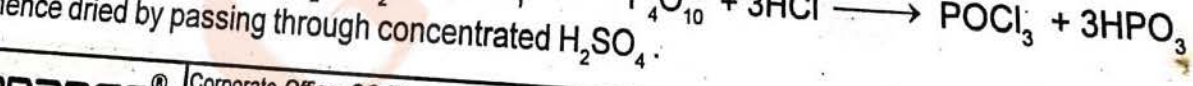
HYDROGEN CHLORIDE (HCl) :

Preparation :

By heating a halide with concentrated acid (Laboratory method) :



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.



HCl is, hence dried by passing through concentrated H_2SO_4 .



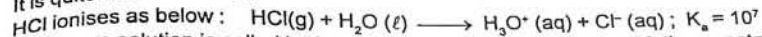
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p-Block Elements (Halogen & Noble Gases)

Properties :

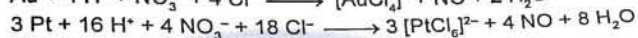
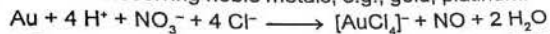
It is a colourless, pungent smelling gases with acidic tastes.

- (i) It is easily liquefied to a colourless liquid (b.p. 189 K) and freezes to a white crystalline solid (f.p. 159 K).
- (ii) It is quite soluble in water.



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

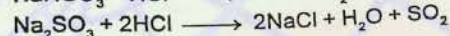
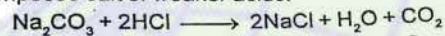
When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.



It reacts with ammonia forming white fumes of NH_4Cl



- (iv) It decomposes salt of weaker acids.



Uses :

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

BLEACHING POWDER :

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

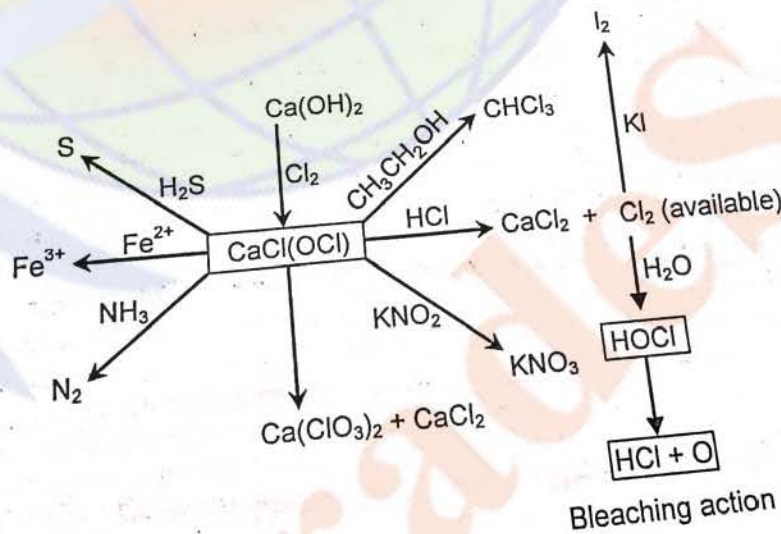
The composition of bleaching powder is $\text{Ca(OCl)}_2 \cdot \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O}$.

PREPARATION:



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.



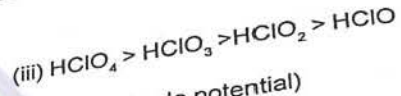
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MAIN PHN - 6

p-Block Elements (Halogen & Noble Gases)
OXY-ACIDS OF Halogens :

Fluorine forms only one oxoacid, HOF due to high electronegativity and small size. Other halogens form a number of oxoacids which are stable only in aqueous solutions or in the form of their salts. They can not be isolated in pure form.

Halic (I) acid (Hypohalous acid)	HOF (Hypofluorous acid)	HOCl (Hypochlorous acid)	HOBBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic (III) acid (Halous acid)	-	HOCIO (chlorous acid)	-	-
Halic (V) acid (Halic acid)	-	HOCIO ₂ (chloric acid)	HOBRO ₂ (bromic acid)	HOIO ₂ (iodic acid)
Halic (VII) acid (Perhalic acid)	-	HOCIO ₃ (perchloric acid)	HOBRO ₃ (perbromic acid)	HOIO ₃ (periodic acid)



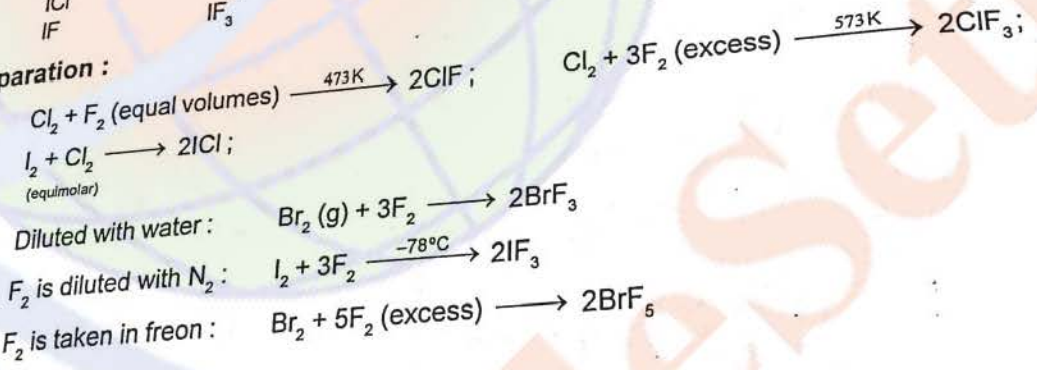
- Some important order**
- (a) Acid strength
(i) $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ (ii) $\text{HOCl} > \text{HOBr} > \text{HOI}$
 - (b) Oxidising powder
(i) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ (ii) $\text{BrO}_4^- > \text{IO}_4^- > \text{ClO}_4^-$ (According to electrode potential)
 - (c) Order of disproportionations
 $3 \text{XO} \longrightarrow 2\text{X}^- + \text{XO}_3^-$ (hypohalite ion); $\text{IO}^- > \text{BrO}^- > \text{ClO}^-$

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.

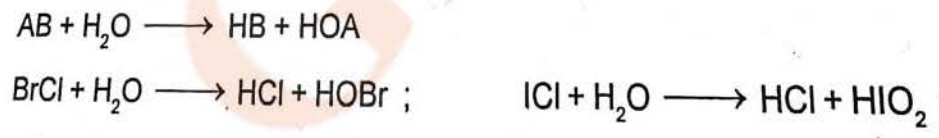
AB	AB ₃	AB ₅	AB ₇
ClF	ClF ₃	ClF ₅	IF ₇
BrF	BrF ₃	BrF ₅	
ICl	ICl ₃	IF ₅	
IF	IF ₃		

Preparation :



Properties :

- (i) These compounds may be gases, liquids or solids.
Gases : ClF, BrF, ClF₃, IF₇; Liquids : BrF₃, BrF₅; Solids : ICl, IBr, IF₃, ICl₃.
- (ii) All interhalogens are covalent molecules and are diamagnetic in nature since all the valence electrons present as bonding or non-bonding electrons are paired.
- (iii) The boiling points increases with the increase in the electronegativity difference between A and B atoms.
- (iv) Interhalogen compounds are more reactive than the parent halogens but less reactive than F_2 .
- (v) Hydrolysis : All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when AB), halite (when AB₃), halate (when AB₅), and perchalate (when AB₇) anion derived from the larger halogen.



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