

B.Sc. Part-I (Hons.), Paper: IB (Inorganic Chemistry)

Group 17, Unit-1: Chemistry of Halogens. [By Dr. Birendra Kumar, Maharaja College]

Group-17 of modern periodic table consists of six elements: Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I), Astatine (At) & Tennessine (Ts). First four elements (F, Cl, Br, I) are known as halogens (halo = salt + gen = producing). They belong to p-block.

* Electronic Conf. & Oxidation states: Group-17 elements have electronic configurations:
 $F_9: [He] 2s^2 2p^5$; $Cl_{17}: [Ne_{10}] 3s^2 3p^5$; $Br_{35}: [Ar_{18}] 3d^{10} 4s^2 4p^5$; $I_{53}: [Kr_{36}] 4d^{10} 5s^2 5p^5$
 $At_{85}: [Xe_{54}] 4f^{14} 5d^{10} 6s^2 6p^5$; $Ts_{117}: [Rn_{86}] 5f^{14} 6d^{10} 7s^2 7p^5$

Outer electronic Conf. = $ns^2 np^5$ ($n=2$ to 7) So, they have seven electrons in their outershell, and they either gain an electron by forming anion (X^-) or a covalent bond in order to complete their octet.

Oxidation states exhibited by Group-17 elements (Halogens) are as follows:

Element	Outer Elk. Conf.	Oxidation states
Fluorine (F)	$2s^2 2p^5$	-1
Chlorine (Cl)	$3s^2 3p^5$	-1, +1, +3, +4, +5, +6, +7
Bromine (Br)	$3d^{10} 4s^2 4p^5$	-1, +1, +3, +4, +5, +6
Iodine (I)	$4d^{10} 5s^2 5p^5$	-1, +1, +3, +5, +7

Fluorine (F) is most electronegative element, so it always univalent (-1). Among the other halogens, oxidation states +1, +3, +4 & +7 are possible. These 0 states (higher) arise by unpairing of s & p-electrons to empty d-orbitals. These oxidation states found in the oxides, oxyacids, oxy salts of halogens & interhalogens. The oxidation states +4 & +6 are apparently anomalous and occur in the oxides: ClO_2, BrO_2, Cl_2O_6 & BrO_3 .

* Preparation/Isolation/Production: Fluorine gas is prepared by electrolysis of fluorides in media with no other anions present. The most commonly used electrolytes are $KF \cdot 2HF$ melted at $70-100^\circ C$ or $KF \cdot HF$, melted at $250-270^\circ C$. The molten mass is taken in cell made of steel/copper/monel metal coated with an unreactive layer of F, steel/copper cathodes and ungraphitized carbon anodes are used. $KF \cdot HF \xrightarrow[250-270^\circ C]{(solid)}$ $KF \cdot HF \xrightarrow[Electrolysis]{(molten)}$ $F_2 + H^+$
 At cathode: $H^+ + e \rightarrow H \rightarrow \frac{1}{2} H_2 \uparrow$; At anode: $F^- - e \rightarrow F \rightarrow \frac{1}{2} F_2 \uparrow$

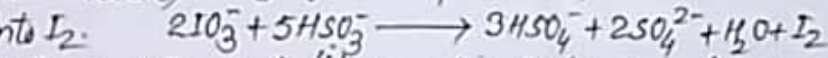
Chlorine gas is produced in large quantities by the electrolysis of aqueous NaCl solution (brine) in the manufacture of NaOH (caustic soda) or fused NaCl in the manufacture of sodium (Na) metal. $NaCl + H_2O \xrightarrow{Electrolysis} Na^+ + Cl^- + H^+ + OH^-$; At cathode: $H^+ + e \rightarrow \frac{1}{2} H_2 \uparrow$
 At anode: $Cl^- - e \rightarrow Cl \rightarrow \frac{1}{2} Cl_2 \uparrow$; $Na^+ + OH^- \rightarrow NaOH$

$NaCl \xrightarrow{Electrolysis} Na^+ + Cl^-$; At cathode: $Na^+ + e \rightarrow Na$; At anode: $Cl^- - e \rightarrow \frac{1}{2} Cl_2 \uparrow$
 Now, Chlorine is produced by Deacon process as follows: $2HCl + \frac{1}{2} O_2 \xrightarrow[400^\circ C]{CuCl_2 catalyst} H_2O + Cl_2 \uparrow$

Bromine is obtained electrolysis of bromide salts or by passing Cl_2 into sea water at pH 3.5, bromide ions present is oxidized into Br_2 . $2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2$. The bromine is absorbed in Na_2CO_3 solution, giving a mixture of $NaBr$ & $NaBrO_3$, when these are acidified and distilled, pure bromine obtained. $HBrO_3 + 5HBr \rightarrow 3Br_2 + 3H_2O$

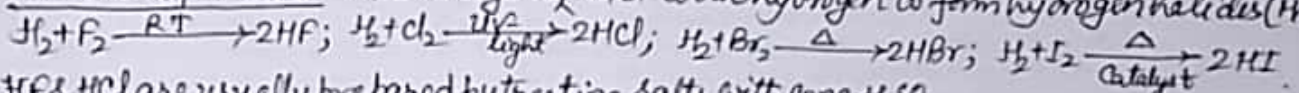
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Iodine is obtained from Chile salt petre, which contains mainly NaNO_3 and traces of NaIO_3 (sodium iodate) & Na_5IO_6 (sodium periodate). The iodate concentrate is reduced by NaHSO_3 into I_2 .

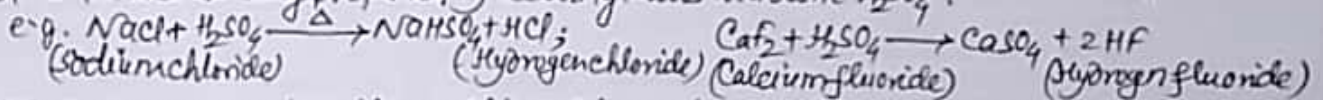


* General properties & Reactivity: (i) All exist as diatomic molecules (X_2). The bond energy ($E_{\text{X-X}}$) would be expected to decrease as the atoms become larger due to less effective overlap of orbitals. (ii) Their melting & boiling points increase with the atomic no. increase. F_2, Cl_2 are gases, Br_2 is liquid and I_2 is solid. (iii) I.E. & E.A. values decrease from F to I. F is most electronegative. Cl has highest electron affinity. (iv) All halogens are coloured. F_2 is yellow, Cl_2 is pale green, Br_2 is brown & I_2 is violet. (v) They are strong oxidising agents, and order is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. (vi) They are highly reactive, order of reactivity: $\text{F} > \text{Cl} > \text{Br} > \text{I}$. Fluorine is most reactive due to low F-F bond energy, extremely high oxidising power, smaller sized high electronegativity. Cl & Br react with most of the elements but less vigorously than F. I is less reactive.

* Formation of halides: All halogens react with hydrogen to form hydrogen halides (HX).



HF & HCl are usually prepared by treating salts with conc. H_2SO_4 .



HBr & HI are not prepared by reaction of bromide or iodide & conc. H_2SO_4 since conc. H_2SO_4 oxidizes them into Br_2 & I_2 respectively. HBr can be prepared by the action of H_3PO_4 on a bromide. $3\text{KBr} + \text{H}_3\text{PO}_4 \longrightarrow \text{K}_3\text{PO}_4 + 3\text{HBr}$; $3\text{KI} + \text{H}_3\text{PO}_4 \longrightarrow 3\text{HI} + \text{K}_3\text{PO}_4$.

In laboratory, HBr & HI is prepared by adding Br_2 or I_2 solution to a mixture of red phosphorus and water. $2\text{P} + 3\text{Br}_2 \longrightarrow 2\text{PBr}_3$; $\text{PBr}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HBr}$.

Property: HCl, HBr & HI are gases, but HF is a liquid with low boiling point (19°C) due to intermolecular hydrogen bonding.

In gaseous state, the hydrides (HX) are essentially covalent, but in aqueous solutions they ionize and function as strong acids. e.g. $\text{HCl} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$. In aqueous solution HF is only slightly ionized. Order of acidic strength: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

Hydrogen halides are reducing property agents. Order of reducing prop: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

Solutions of HF are very corrosive, but surprisingly little corrosion occurs at conc. $> 80\%$.

Uses: HF is used to make fluorocarbons (freons), which are used in aerosols.

Anhydrous HF is a catalyst for making long chain alkyl benzenes which are subsequently converted to sulphonates and used as detergents. Aqueous HF is used for etching glass, pickling steel and making fluorides e.g. $\text{AlF}_3, \text{BF}_3$ etc. liquid HF has been used as a non-aqueous solvent especially for preparation of fluoro complexes. HCl is used for the production of vinyl chloride and chlorinated solvents. It is used in acidimetry-alkalimetry titrations and as laboratory reagent.

HBr & HI are used as reducing agents