

Halogen Family.

Fluorine is the first member of group 17 or VIIA of the periodic table. It consists of five elements Fluorine (F), Chlorine (Cl), bromine (Br), iodine (I) and astatine (At). These are known as halogen because their salts are found in sea water. Halogen is a Greek word meaning a sea salt.

Electronic configuration

Elements	Electronic configuration ($ns^2 np^5$)
${}_9F$	$1s^2, 2s^2 2p^5$ or $[He]2s^2 2p^5$
${}_{17}Cl$	$1s^2, 2s^2 2p^6, 3s^2 3p^5$ or $[Ne]3s^2 3p^5$
${}_{35}Br$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^5$ or $[Ar]3d^{10} 4s^2 4p^5$
${}_{53}I$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^5$ or $[Kr]4d^{10} 5s^2 5p^5$
${}_{85}At$	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^5$ or $[Xe]4f^{14} 5d^{10} 6s^2 6p^5$

Physical properties

(1) **Physical state:** Halogens exist as diatomic covalent molecules.

F_2 – gas, Cl_2 – gas, Br_2 – corrosive liquid, I_2 – volatile solid.

(2) **Melting and boiling points:** They increase with increase in atomic number.

(3) **Ionization energy:** The I.E. decreases on moving down the group.

(4) **Electron affinity:** $F < Cl > Br > I$ or $Cl > F > Br > I$.

(5) **Electronegativity:** $F > Cl > Br > I$.

(6) **Bond energy**

Element	F – F	Cl – Cl	Br – Br	I – I
Bond length (Å)	1.42	1.99	2.28	2.67
Bond dissociation energy (kcal / mole)	38	57	45.5	35.6

(7) **Colour:** F – Light yellow, Cl – Greenish yellow, Br – Reddish brown, I – Deep violet.

(8) **Oxidation state:** All exhibit –1 Oxidation state Except fluorine other element also show +3, +5, +7 oxidation state.

(9) **Oxidising power:** $F_2 > Cl_2 > Br_2 > I_2$.

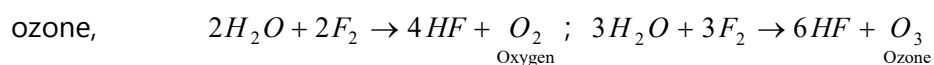
(10) **Solubility:** Halogen being non-polar in nature do not dissolve in water

$2F_2 + 2H_2O \rightarrow 4HF + O_2$, $3F_2 + 3H_2O \rightarrow 6HF + O_3$ (fluorine highly soluble) Cl_2 and Br_2 are fairly soluble. I_2 is a least soluble in water.

Chemical properties

(1) **Reactivity:** The halogen are most reactive elements due to their low bond dissociation energy, high electron affinity and high enthalpy of hydration of halide ion. $F > Cl > Br > I$

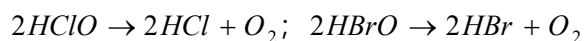
(2) **Reaction with H₂O:** Halogens readily decomposes water. This tendency decreases on moving down the group. Fluorine decomposes water very energetically to give oxygen and ozone,



Fluorine gives fumes in moist air. This is due to the formation of HF, which is a liquid and can absorb moisture to form liquid droplets and therefore, gives fumes with moist air. Chlorine and bromine react less vigorously, $Cl_2 + H_2O \rightarrow HCl + \underset{\text{Hypochlorous acid}}{HClO}$;



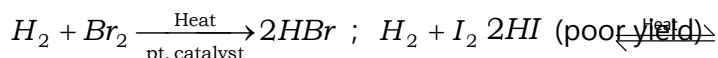
In the presence of sunlight, HClO (hypochlorous acid) HBrO (hypobromous acid) liberate oxygen.



Iodine is only slightly soluble in water. However, it dissolves in 10% aqueous solution of KI due to the formation of I_3^- ions. $\text{I}_2 + \text{KI} \rightleftharpoons \text{KI}_2$ or $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$

Complex ion

(3) **Reaction with hydrogen:** Form covalent halides.



Acidic strength in aqueous solution is in the order, $\text{HI} > \text{HBr} > \text{HCl} < \text{HF}$.

Reducing character of hydrides follow the order, $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

Boiling point $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$. Thermal stability, $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$.

HCl is also called Muriatic acid.

(4) **Hydrides:** All the halogens combine directly with hydrogen to form halogen acids but their reactivity progressively decreases from fluorine to iodine, $\text{H}_2 + \text{X}_2 \rightarrow 2\text{HX}$ (X = F, Cl, Br or I).

(i) **Boiling points or volatility:** In other words volatility decreases in the order: $\text{HCl} > \text{HBr} > \text{HI} > \text{HF}$ as the boiling points increase in the order : $\text{HCl} (189\text{K}) < \text{HBr} (206\text{K}) < \text{HI} (238\text{K}) < \text{HF} (292.5\text{K})$.

(ii) **Thermal stability:** Thermal stability of the hydrides decrease from HF to HI i.e., $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$.

(iii) **Acidic strength:** The acidic strength of halogen acids decreases from HI to HF i.e., $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

(iv) **Reducing properties:** Since the stability of hydrides decreases from HF to HI, their reducing properties increase in the order $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

(v) **Dipole moments:** The dipole moments of hydrogen halides decrease in the order : HF > HCl > HBr > HI as the electro negativity of the halogen atom decreases from F to I.

HX	HF	HCl	HBr	HI
Dipole moment (D)	1.74	1.07	0.78	0.38

(5) **Oxides:** Halogens (except F₂) do not combine readily with oxygen. However, a number of compounds of halogens with oxygen have been prepared by indirect methods. Only two compounds of fluorine with oxygen, i.e. oxygen difluorine (OF₂) and oxygen fluoride (O₂F₂) are known. Chlorine forms largest number of oxides i.e. Cl₂O, ClO₂, Cl₂O₆ and Cl₂O₇ while iodine forms the least, i.e. I₂O₅. Bromine, however, forms three oxides (Br₂O, BrO₂ and BrO₃). In all these compounds, bonds are largely covalent. All the oxides of halogens are powerful oxidizing agents. These compounds are very reactive and are unstable towards heat. The stability of oxides is greatest for iodine while bromine oxides are the least stable. For a particular halogen, higher oxides are more stable than the lower ones.

Iodine-oxygen bond is stable due to greater polarity of the bond (due to larger electro negativity difference between I and O) while in chlorine-oxygen bond, the stability is gained through multiple bond formation involving the d-orbital of chlorine atom. Bromine lacks both these characteristics and hence forms least stable oxides.

Oxides of chlorine, bromine and iodine are acidic and the acidic character increases as the percentage of oxygen increases in them.

Iodine also forms I₂O₄ and I₄O₉ compounds which are believed not to be true oxides but are basic iodyl iodate, IO (IO₃) and normal iodine triiodate, I (IO₃)₃ having tripositive iodine as the cation.

OF₂ is V-shaped having bond angle 103°, Cl₂O is also V-shaped with bond angle 111° while ClO₂ is angular with bond angle 118°. It is paramagnetic due to odd number of electrons having three-electron bond. It is regarded as a mixed anhydride of chloric and chlorous acids. 2ClO₂ + H₂O → HClO₂ + HClO₃

(6) **Oxoacids of halogens:** Fluorine does not form any oxoacid since it is the strongest oxidizing agent. Chlorine, bromine and iodine mainly form four series of oxoacids namely hypohalous acid (HXO), halous acid (HXO₂) halic acid (HXO₃) and perhalic acid (HXO₄) as given below:

Oxidation state	Chlorine	Bromine	Iodine	Thermal stability and acid strength	Oxidising power
+1	HClO	HBrO	HIO	Increases ↓	Decreases ↓
+3	HClO ₂	—	—		
+5	HClO ₃	HBrO ₃	HIO ₃		
+7	HClO ₄	HBrO ₄	HIO ₄		
	Acidity decreases →				

(i) **Hybridized ion:** In all these oxoacids, the halogen atom is sp^3 -hybridized.

(ii) **Acidic character:** All these acids are monobasic containing an—OH group. The acidic character of the oxoacids increases with increase in oxidation number, i.e., $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ and the strength of the conjugate bases of these acids follows the order, $\text{ClO}^- > \text{ClO}_2^- \rightarrow \text{ClO}_3^- > \text{ClO}_4^-$.

(iii) **Oxidising power and thermal stability:** The oxidizing power of these acids decreases as the oxidation number increases, i.e., $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$. Stability of oxoacids of chlorine in the increasing order is, $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ and the increasing stability order of anions of oxoacids of chlorine is, $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$.

As the number of oxygen atoms in an ion increases there will be a greater dispersal of negative charge and thus greater will be the stability of ion formed. For different halogen having the same oxidation number, the thermal stability decreases with increase in atomic number i.e., it is in the order $\text{HClO} > \text{HBrO} > \text{HIO}$ and $\text{ClO}^- > \text{BrO}^- > \text{IO}^-$. However, in HXO_3 is most stable. The stability order being $\text{HClO}_3 < \text{HBrO}_3 < \text{HIO}_3$.

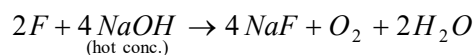
(iv) Perhalates are strong oxidizing agents, the oxidizing power is in the order,



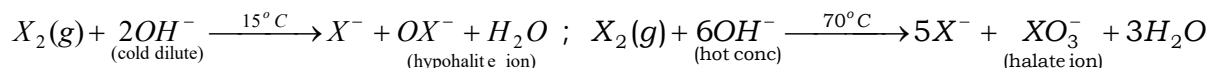
Thus BrO_4^- is the strongest oxidizing agent (though its reaction is quite slow) and ClO_4^- is the weakest.

(v) The acidity of oxoacids of different halogens having the same oxidation number decreases with increase in the atomic size of the halogen i.e. $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$.

(7) **Reaction with alkalis:** $2F_2 + 2NaOH \xrightarrow{\text{(cold dilute)}} 2NaF + OF_2 + H_2O$;

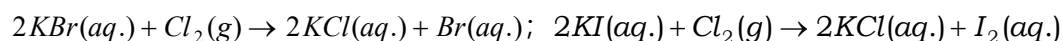


Halogen other than fluorine (Cl_2, Br_2, I_2) react with NaOH as follows,



(8) **Bleaching action of halogen:** Cl_2 acts as bleaching agent, its bleaching action is permanent Cl_2 water can also act as ink remover.

(9) **Reaction with other halides**



(10) **Inter halogen compounds:** The compounds of one halogen with the other are called interhalogens or interhalogen compounds. The main reason for their formation is the large electronegativity and the size differences between the different halogens. Taking A as the less electronegative and B as the more electronegative halogen, they are divided into the following four types the less electronegative halogen (A) is always written first.

AB	AB ₃	AB ₅	AB ₇
ClF BrF, BrCl, ICl IBr, IF	ClF ₃ , BrF ₃ IF ₃ , ICl ₃	BrF ₅ , IF ₅	IF ₇

These interhalogen compounds are unstable and more reactive

(i) **General properties**

(a) Largest halogen always serves the central atom.

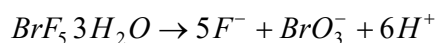
(b) The highest interhalogen compound i.e. IF₇ is obtained with iodine, the largest halogen attached to the smallest one

(c) The bonds in interhalogen compounds are essentially covalent.

(d) Thermal stability decreases as the size difference decreases and increases as the polarity of the bond increases. Thus ClF is thermally more stable as compared to IBr.

(e) They ionize in solution or in the liquid state, $2ICl \rightleftharpoons I^+ + ICl_2^-$; $2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$

(f) Hydrolysis of interhalogen compounds always produces a halide ion derived from smaller halogen and oxyhalide derived from larger halogen, $ICl + H_2O \rightarrow Cl^- + IO^- + 2H^+$;



(g) They are strong oxidizing agents.

(h) Largest number of interhalogens are formed by fluorine due to its smaller size and higher electronegativity or oxidizing power.

(ii) **Structure:** Interhalogen compounds are,

(a) AB type i.e. ICl, IBr, IF etc, are linear

(b) AB₃ type i.e. IF₃, ClF₃, BrF₃ have distorted trigonal bipyramidal (dsp³-hybridization) structures of T-shape due to two lone pairs in equatorial positions ICl₃ is dimeric, I₂Cl₆ and has a planar structure.

(c) AB₅ types i.e. BrF₅, IF₅ have distorted octahedral (d²sp³-hybridization) shapes or square pyramidal due to a lone pair one of the axial positions.

(d) AB₇ type i.e. IF₇, have pentagonal bipyramidal (d³sp³-hybridization) structures.

(11) **Polyhalides:** $KI + I_2 \rightarrow KI \rightleftharpoons K^+ + I_3^-$; $Cl_3^-, Br_3^-, I_3^-, ICl_2^-, IBr_2^-, ICl_4^-, BrF_4^-, I_5^-, IF_6^-$ and I_7^-

(12) **Pseudohalogen and pseudohalides**

Pseudohalogen	Pseudohalide
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Cyanogen – $(CN)_2$	Cyanide – CN^-
Oxocyanogen – $(OCN)_2$	Cyanate – OCN^-
Thiocyanogen – $(SCN)_2$	Thiocyanate – SCN^-
Selenocyanogen – $(SeCN)_2$	Selenocyanate – $SeCN^-$

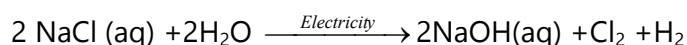
(13) **Freons:** Freon –11 is CCl_3F ; Freon –12 is CCl_2F_2 and it is marketed under the popular brand names such as 'Freon' and 'Genetron'; Freon –113 is $CCl_2F.CClF_2$; Freon –114 is $CClF_2.CClF_2$; Freon –115 is $CClF_2.CF_3$. These cause ozone depletion.

Preparation of halogens

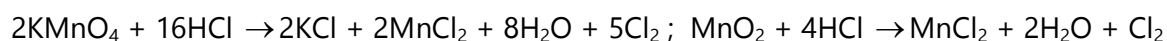
(1) **Preparation of fluorine :** F_2 is prepared by electrolysis of a solution of KHF_2 (1 Part) in HF (5 part) in a vessel (Modern method) made of Ni – Cu alloy or Ni –Cu– Fe alloy called the monel metal using carbon electrodes. During the electrolysis following reactions occur, $KHF_2 \rightleftharpoons KF + HF$; $KF \rightleftharpoons K^+ + F^-$.

At cathode : $K^+ + e^- \rightarrow K$; $2K + 2HF \rightarrow 2KF + H_2 \uparrow$; At anode : $F^- \rightarrow F + e^-$; $F + F \rightarrow F_2$

(2) **Preparation of chlorine:** On the industrial scale, Cl_2 is prepared by the electrolysis of concentrated aqueous solution of NaCl. In this process, NaOH and H_2 are by products.



In the laboratory, Cl_2 can be prepared by adding conc HCl on $KMnO_4$ or MnO_2 .



(3) **Preparation of Bromine:** In laboratory it is prepared by heating NaBr with MnO_2 and Conc H_2SO_4 .



(4) **Preparation of Iodine** (Lab method): By heating a mixture of MnO_2 , H_2SO_4 and an iodide



I_2 is commercially prepared from sea weeds.

Uses of Halogens

(1) **Uses of Fluorine:**

(i) It is used as an oxidizing agent and fluorinating agent. (ii) Fluorine and its compounds such as NF_3 , OF_2 are used as rocket fuels. (iii) It is used in the manufacture of a plastic known as Teflon $(\text{CF}_2-\text{CF}_2)_n$ which is resistant to the action of all acids, alkalies and even boiling aqua regia. (iv) It is used in the manufacture of fluorocarbons like freon which is used as an excellent refrigerant and in air conditioning. (v) It is used for the preparation of uranium hexafluoride, which is used for the separation of isotopes of U(235) and U(238).

(2) **Uses of Chlorine:**(i) Chlorine is used in sterilization of drinking water. (ii) Large quantities of chlorine are used industrially for the bleaching of cotton, paper, wood, textiles, etc. (iii) It is used in making insecticides like D.D.T., germicides, dyes, drugs, etc. (iv) It is used for preparing vinyl chloride which is a starting material for making the plastic PVC. (v) It is used in the manufacture of chlorinated organic solvents like CHCl_3 , CCl_4 , which are used for dry cleaning and degreasing machinery. (vi) It is used in the preparation of HCl, bleaching powder, chlorates, perchlorates, sodium hypochlorite which are important industrial compounds.

(3) **Uses of Bromine:**

(i) Bromine is used in the preparation of ethylene bromide, which is mixed with tetraethyl lead (TEL) and added to the petrol as an anti-knocking agent.
(ii) In the manufacture of AgBr used in photography.
(iii) In the manufacture of dyes, drugs, etc.
(iv) It is used in the manufacture of benzyl bromide which is an effective tear gas.
(v) It is used as a laboratory reagent.

(4) **Uses of Iodine:**

(i) Iodine is used as a laboratory reagent.
(ii) It is used in making medicines and dyes. Tincture of iodine is an antiseptic.
(iii) AgI is used in photographic emulsions.
(iv) It is used in the preparation of iodized salt. Iodized salt is used to prevent the occurrence of common goiter.