HALOGEN FAMILY

1. HALO : SEA SALTS

because they are sea salts forming elements.

$$\left.\begin{array}{l}\text{F}\\ \text{Cl}\\ \text{Br}\\ \text{I}\\ \text{At}\end{array}\right\} ns^2np^5$$

2. IMPORTANT POINT

At (astatine) is a radioactive element.

3. GENERAL PROPERTIES

3.1 State and Nature :

(a) F and Cl are Gas.
(b) Br : Liquid
(c) I, At is solid
(d) All are non metallic

F
I non metallic character decreases down the gp.

(e) I has metallic lustre on heating, I undergoes sublimation.

3.2 Atomic Radii, Ionic Radii, Boiling point and Melting point pt., Density :

All these character increases down the group

3.3 I.P. and E.N.

↓ decreases down the group

3.4 Electron Affinity (E.A.) :

From F to Cl $\longrightarrow$ E.A (↑) due to availability of vacant d-orbital in Cl and then it decrease

So order Cl > F > Br > I.

3.5 Colour properties :

(a) F : Pale yellow
Cl : Greenish yellow
Br : Red
I : Voilet purple.

(b) They have mainly due to ns^2 np^5 configuration. Unpaired e^- are present and visible light is absorbed and excitation of e^- occurs and exhibit colour.

(c) F absorbs violet colour light and appears yellow. It will absorbs yellow coloured light and appears violet.

(d) Astatine being stable could have absorbed orange or red light and would have exhibited indigo or bluish colour.

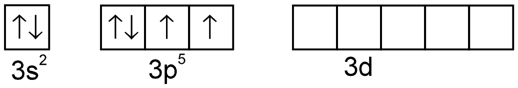
(e) Greenish yellow colour of chlorine and red colour of bromine.

3.6 Valency and Oxidation state :

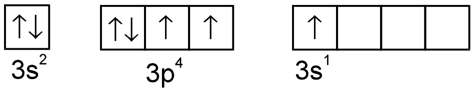
(a) ns^2 np^5

(b) valency = 1
if Halogens combines with more E.N. elements then O.S. = + 1.

(c) For Cl. Ground State :
Valency = 1



1^{st}.E.S.



sp^3d Trigonal bipyramidal.

3.7 Bond Energy :

F – F bond dissociation energy is less than that of Cl – Cl and Br – Br. It is due to larger inter electronic (electron - electron) repulsion between the non bonding electrons in the 2P orbitals of fluorine atom. then these in the 3p orbitals of chlorine atoms.

F – F	Cl – Cl	Br – Br	I – I
38 kcal/mil	57 kcal/mol	45.5 kcal/mol	35.6 kcal/mol

$Cl_2 > Br_2 > F_2 > I_2$

3.8 Oxidising Power :

The electron affinity, or tendency to gain electrons reaches a maximum at chlorine. Oxidation may be regarded as the removal of electron so that an oxidising agent gains electrons.

Thus the halogens act as oxidizing agents.

The strength of an oxidising agent (i.e. oxidation potential) depends upon several energy terms and represented by following diagram.

$$\frac{1}{2}X_2\,(s) \xrightarrow[\text{Fusim}]{\frac{1}{2}\text{ Heat}} \frac{1}{2}X_2(\ell) \xrightarrow[\text{Evaporation}]{\frac{1}{2}\text{ heat}} \frac{1}{2}X_2(g)$$

$$\xrightarrow[\text{Dissociation}]{\frac{1}{2}\text{ heat}} X(g) \xrightarrow[\text{affinity}]{\text{Electron}} X^-(g) \xrightarrow[\text{hydration}]{\text{heat of}} X^-\text{ (hydrated)}$$

oxidation potential (E^0)

The heat of fusion, evaporation and dissociation are positive and electron affinity and heat of hydration are negative. The net energy (E) required for oxidising reaction is given by -

$$E_{(net)} = \frac{1}{2}H_f + \frac{1}{2}H_v + \frac{1}{2}H_d - E.A. - H_{(hyd)}$$

Element	E_{net} (kcal)
F_2	– 186.5
Cl_2	– 147.4
Br_2	– 136.4
I_2	– 122.4

Thus oxidising powers decrease on descending in group VII. Fluorine is so strong oxidising agent that H oxidizes water to oxygen. The oxidation of H_2O by Cl_2 is thermodynamically possible but since the energy of activation is high this reaction does not occur.

$$F_2 + H_2O \longrightarrow 2H^+ + 2F^- + \frac{1}{2}O_2$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

Iodine is even weaker oxidising agent and the free energy change indicate that energy would have to be supplied to make it oxidise water.

4. CHEMICAL PROPERTIES

4.1 Reaction with H_2 :

All hologens reacts with H to form hydrogen halides.

(a) $F_2 + H_2 \xrightarrow{\text{Dark}} H_2F_2$

$Cl_2 + H_2 \xrightarrow{\text{Light}} 2HCl$

$Br_2 + H_2 \xrightarrow{\Delta} 2HBr$

$I_2 + H_2 \xrightarrow{\Delta} 2HI$

(b) Reactivity of Halogens F > Cl > Br > I

(c) HCl in gaseous state is hydrogen chloride. While HCl in aqueous solution is hydrochloric acid.

(d) HCl, HBr, HI acts as reducing agent.

(e) H_2F_2 cannot decompose into H_2 and F_2 and so its can never acts as reducing agent.

(f) H_2F_2 has highest boiling point and exist in liquid state.

(g) HCl , HBr and HI exist on gaseous state.

(h) HCl b.p. is very low and after HCl b.p. increases because Vanderwaals forces increases (↓) and so b.p. (↑).

4.2 Reaction With H_2O :

(a) H_2O acts as reducing Agent only with F.

$2F_2 + 2H_2O \longrightarrow 2H_2F_2 + O_2$

(b) $Cl_2 + H_2O \longrightarrow HCl + HClO$ Hypochlorous acid $\xrightarrow{\text{Light}} HCl + [O]$

So Cl_2 in presence of moisture acts as bleaching agent.

(c) $H_2O + I_2 \longrightarrow$ No Reaction.

(d) All these halogen are soluble in water except I_2 when KI solution is added I_2 will also dissolve because adsorption of I_2 molecule on the surface of iodide ion KI_3 is formed which is a highly ionic compound.

4.3 Displacement Reaction :

(a) $F_2 + 2NaX \longrightarrow 2NaF + X_2$ {X = Cl, Br, I}

$Cl_2 + 2NaX \longrightarrow 2NaCl + X_2$ {X = Br_2, I_2}

So order of displacement [$F_2 > Cl_2 > Br_2 > I_2$]

(b) If Halogen is in –ve O.S. then it is replaced by more E.N. element.

(c) If Halogen is +ve O.S. then it is replaced by less E.N. element.

4.4 Reaction with Metals :

Metal halides are formed F > Cl > Br > I

4.5 Reaction with Non Metals :

Non metallic halides are formed.

Eg. NF_3, PCl_3 etc.

4.6 Reaction with NH_3 :

(a) $3F_2 + NH_3 \longrightarrow NF_3 + 3HF$

(b) $3Cl_2 + NH_3 \longrightarrow NCl_3 + 3HCl$

(c) I_2 is less reactive and so remains same and Ammoniated compound will form.

$3I_2 + 2NH_3 \longrightarrow NI_3 . NH_3 + 3HI$

4.7 Reaction with NaOH :

(a) $F_2 + NaOH \text{ (dil.)} \longrightarrow 2NaF + OF_2 + H_2O$

(b) $2F_2 + 4NaOH \text{ (conc.)} \longrightarrow 4NaF + 2H_2O + O_2$.

They are both redox reactions.

(c) $Cl_2 + NaOH \longrightarrow NaCl + NaClO_3 + H_2O$

(d) $Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O$

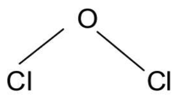
4.8 Formation of Oxides :

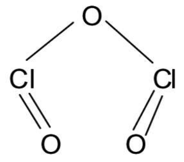
(a) No oxides of F because of its maximum E.N. character.

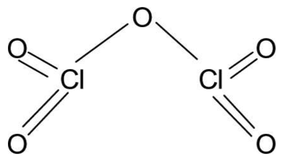
(b) Rest forms

	X_2O	X_2O_3	X_2O_5	X_2O_7
	+ 1	+ 3	+ 5	+ 7
Eg.	Cl_2O	Cl_2O_3	Cl_2O_5	Cl_2O_7

Structure







(c) All these oxides are acidic

(d) Acidity decreases down the group and maximum active oxide is Cl_2O_7

4.9 Formation of Oxyacids :

(a) F does not form any oxyacid because High E.N.

(b) Rest oxyacids are

HXO	HXO_2	HXO_3	HXO_4
+1	+ 3	+ 5	+ 7

Note : Hypo halous acid Halous acid Halic acid Perhalic acid

(c) All these oxy acids are acidic

(d) Acidity and thermal stability decreases down the group and maximum acidity and thermal stability will be of $HClO_4$.

(e) Thermal stability of acids increases with the increasing O.S. of the halogens or with increase in the no. of oxygen atom.

(f) Oxidising Power :

(i) All these oxyacids acts as strong oxidizing agents.

(ii) Stability of anions increases from ClO^- to ClO_4^-, the oxidising power decreases from ClO^- to ClO_4^-

(iii) Order of oxidising agent $HClO > HClO_2 > HClO_3 > HClO_4$

4.10 Miscellaneous Reaction :

(a) $I_2 + Na_2S_2O_3 \text{ (Hypo)} \longrightarrow 2NaI \text{ (Colourless)} + Na_2S_4O_6$

This reaction is employed for identification of I_2.

(b) Dry $Cl_2 + Ca(OH)_2(s) \longrightarrow CaOCl_2$ (Bleaching Powder) + H_2O

4.11 Inter Hologens :

Product obtained by uniting two halogen compounds :

AB AB$_3$ AB$_5$ AB$_7$

Where A = less E.N. Halogen

B = More E.N. Halogen

Eg.	ClF	ClF_3	BrF_5	IF_7
	$BrCl$	$BrCl_3$	ICl_5	
	IBr	IBr_3		

These interhalogens have polarity because of different E.N.

Note : Abnormal Behaviour of Fluorine as Compared to Other Members :

Fluorine differs considerably from other halogens due to -

(i) Small size

(ii) High electronegativity.

(iii) Non availability of d - orbitals in its valency shell.

(iv) Low bond dissociation energy of F – F bond.

(a) Boiling point of HF is the highest and for other increases down the group.

(b) Due to hydrogen bonding HF is a liquid while HCl, HBr and HI are gases.

(c) Fluorine, being the most electronegative gives SF_6 while other member do not form hexahalides with sulphur.

(d) It exhibits oxidation state of only –1.

(e) It is the strongest oxidising agent.

(f) It liberates oxygen as well as ozone with water.

(g) HF does not ionize while HCl, HBr and HF ionize in aqueous solution.

(h) Solubility of salts :

(i) AgF is soluble in water while AgCl, AgBr and AgI are insoluble.

(i) It combines with hydrogen with explosion at a low temperature and even in the dark. No other halogens combines so readily.

$H_2 + F_2 \longrightarrow 2HF$

(j) It liberates oxygen as well as ozone with water.

$$2H_2O + 2F_2 \longrightarrow 4HF + O_2$$
$$3H_2O + 3F_2 \longrightarrow 6HF + O_2$$

5. FAMILY MEMBERS OF HALOGEN

5.1 Fluorine (F_2) :

(i) Uses :

It is used in the preparation of fluorine compound such as.

(a) Freon : Fereon - 12 i.e. CF_2Cl_2 as used in refrigeration and air conditioning in place of NH_3 and SO_2.

(b) Teflon : $(-F_2C-CF_2)_n$ It is a new plastic.

5.2 Chlorine (Cl_2) :

(i) Preparation :

(a) By the electrolysis of brine (Aq. solution of NaCl) in nelson cell. This is the cheapest method

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At Cathode : $H^+ + e^- \longrightarrow H$

$H + H \longrightarrow H_2$

At anode : $Cl^- \longrightarrow Cl + e^-$

$Cl + Cl \longrightarrow Cl_2 \uparrow.$

(b) Decon's Process :

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2 \uparrow.$$

4 : 1

Chlorine gas thus obtained contains N_2 and O_2 and is used for the manufacture of bleaching powder by hansenclever's process

(c) Lab Method : $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl + 2H_2O$

(ii) Properties :

(a) Bleaching :

$Cl_2 + H_2O \longrightarrow 2HCl + [O]$

Coloured matter + [O] ⟶ Colourless matter.

(iii) Uses :

(a) As a Germicide and disinfectant.

(b) Domestic antiseptic solution (NaOCl)

(c) In Mfg of bleaching powder, D.D.T etc.

(d) In warfare gases such as phosgene $CaOCl_2$, tear gas ($CCl_3 . NO_2$) and mustard gas

($ClC_2H_4 - S - C_2H_4Cl$)

5.3 Bromine (Br_2) :

(i) Preparation :

(a) Bittern : Mother liquar contains about 0.25% of bromine or $MgBr_2$ and is known as bittern.

Britten is treated with Chlorine gas.

$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2.$

(ii) Uses :

(a) it is used in preparation of ethyl bromide which is used in the mfg of tetraethyl lead (TEL) as an importantanti - knock compound in the petroleum industry.

$C_2H_6 + Br_2 \longrightarrow C_2H_5Br + HBr$

$4C_2H_5Br + 4Na - Pb \longrightarrow (C_2H_5)_4 Pb + 4NaBr + 2Pb$

5.4 Iodine (I_2) :

(i) I_2 is the rarest of all the halogens. Its main source is kelp (varee).

(ii) Properties :

(a) It is only sparingly soluble in water but readily soluble in Na or K iodide due to formation of triiodide.

$KI + I_2 \longrightarrow KI_3$

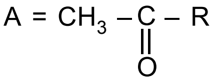
However, this solution behaves as a simple mixture of KI and free I_2.

Note : Tincturc of iodine contains $\frac{1}{2}$ ounce I_2, $\frac{1}{4}$ ounce KI and 1 pinch of rectified spirit.

(b) Iodoform Reaction :

$$2C_2H_5OH + 6KOH + 4I_2 \longrightarrow HCOOK + CHI_3 + 5KI + H_2O$$

Iodoform or Haloform reaction show by following -



$A = CH_3-\underset{\underset{O}{\|}}{C}-R$

When R = H, CH_3, C_2H_5, ...

R = Benzyl and its derivatives

R = Every 2-Alcohol (not secondary)

R = C_2H_5OH (only Ethyl Alcohol in Primary

R = No. tertiary Alcohol.

6. COMPOUNDS OF DIFFERENT MEMBERS

6.1 Potassium Chlorate ($KClO_3$)

(i) On heating with conc. HCl, $KClO_3$ gives a mixture of chlorine and chlorine dioxide known as exchlorine.

$$2KClO_3 + 4HCl \longrightarrow 2KCl + 2ClO_2 + Cl_2 + 2H_2O$$

(ii) Uses :

(a) In mfg. of matches, fire works and photographic flash powders.

6.2 Pseudohalides and Pseudohalogens :

A few ions are known, consisting of two or more electronegative atoms of which at least one is nitrogen, that have properties similar to those of halide ions. These ions are called pseudohalide ions, Pseudohalide ions are univalent and these form salts resembling halide salts.

The pseudohalide ions are :

Cyanide ions (CN^-) : Isocyanide ion (NC^-)

Cyanate ion (OCN^-) : Fulminate ion (ONC^-)

Thiocyanate ions (SCN^-) : Isothiocyanate ion (NCS^-)

Selenocyanate ion ($SeCN^-$) : Tellurocyanate ion ($TeCN^-$)

Azide ion (N_3^-) : Azido carbon disulphide ion ($SCSN_3^-$)

Comparison of [Cl_2, Br_2 and I_2]

S.No.	Property	Chlorine	Bromine	Iodine
1.	Physical State	Gas	Liquid	Solid
2.	Colour of Vapour	Greenish Yellow	Dark Red	Violet
3.	Action of H_2O	Decomposes into HCl & O_2	Decomposes Slowly in Presence of Light	No action
4.	Oxidising Action	Strong	Good	Weak
5.	Bleaching Action	Moist Cl_2 is a Good Bleaching Agent	Moist Br_2 is a good Bleaching Agent	No Bleaching
6.	Action of Halides	Displaces Br_2 & I_2	Displaces I_2	No Action
7.	Combination with H_2	Explosive in Light Slow in Dark	Only on Heating	Heating + Catalyst

As the dimers of halide ions are called halogens, the covalent dimers of the pseudohalide ions are called halogens or halogenoids.The pseudohalogens known are :

Cyanogen $(CN)_2$: Oxycyanogen $(OCN)_2$
Thiocyanogen $(SCN)_2$: Selenocyanogen $(SeCN)_2$
Tellurocyanogen $(TeCN)_2$: Azido carbon disulphide $(SCSN_3)_2$

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

(i) It forms an acid, HCN.

(ii) It can be oxidised to $(CN)_2$ molecule.

(iii) It forms insoluble salts with Ag^+, Pb^{2+} and Hg_2^{2+}.

(iv) It forms large number of complexes similar to halide complexes, e.g.

$[Cu\ (CN)_{4\backslash}]^{2-}$ and $[CuCl_4]^{2-}$. $[Co(CN)_6]^{3-}$ and $[CoCl_6]^{3-}$

(v) Inter-pseudohalogen compounds ClCN, BrCN and ICN can be formed.

(vi) AgCN is insoluble in water but soluble in ammonia like AgCl.

Oxy acids of Halogens

Oxidation state of halogens	Chlorine	Bromine	Iodine	Name of acid	Name of salt	
+1	HClO	HBrO	HIO	Hypohalous	Hypohalite	↓ Stability and acidity increases but oxidising power decreases
+3	$HClO_2$	-	-	Halous	Halite	
+5	$HClO_3$	$HBrO_3$	HIO_3	Halic	Halate	
+7	$HClO_4$	$HBrO_4$	HIO_4	Perhalic	Perhalate	

⟶
Acidity increases

6.3 Oxy Acids of Halogens

(1) Fluorine does not form any oxy-acids because it is more electronegative than oxygen.

(2) Other halogens form four series of oxy acids with formulae

HXO → Hypohalous
HXO_2 → Halous
HXO_3 → Halic
HXO_4 → Perhalic acids or Halic (I), Halic (III), Halic (V) and Halic (VII)

6.4 Some important general trends in Oxy-acids of Halogens

(1) In oxy-acids, hydrogen is present as –OH group

(2) All the hypohalous acids (HXO) are unstable and readily form HXO_3. Among these the relative order of stability is

HClO > HBrO > HIO

(3) In halic acids (HXO_3), iodic acid is the most stable.

(4) Thermal stability -

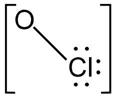
Thermal stability $\propto$ oxidation state of halogens & No. of oxygen atoms.

(a) The thermal stability of both the acids and their salts increases with the increasing oxidation state of the halogen or with the increase in the number of oxygen atoms i.e. stability of the oxy halide anion increases from ClO^-, ClO_2^-, ClO_3^-, ClO_4^-.

(b) This is due to the fact with the increasing number of oxygen atoms in the series, the no. of electron involved in forming σ and π bonds increases.

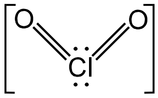
(c) Thus in the most stable perchlorate ion, ClO_4^-, all the valence orbitals and electron of chlorine atom are involved in the formation of bonds.

(d) The stability of perchlorate ion, ClO_4^- may also be said due to greater multiplicity of the Cl-O bond.



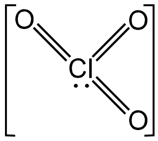
Hypo chlorite

Shape - dumb - bell



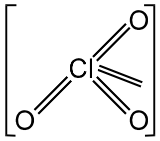
Chlorite

Shape - bent chain



Chlorate

Shape - Pyramidal



Per- chlorate

Shape - Tetrahedral.

(5) Oxidising power -

ClO^-

↓ Stability increases and oxidising power decreases

ClO_4^-

Hypochlorites are the strongest oxidising agents.

(6) Relative acidity $\propto$ oxidation no.

$HClO_4 > HClO_3 > HClO_2 > HClO$

Note : (i) In all these acids and salts halogen is in sp^3 hybridised state.

(ii) Stronger the acid, the weaker will be its conjugate base and vice-versa.

$ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$ (relative basic character)

Thus ClO_4^- is the weakest base and $HClO_4$ (conjugate acid of ClO_4^-) is the strongest acid.

$ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$

$\longleftarrow$

Relative stability of Cl–O bonds