Atomic Energy Central School-3 Tarapur

- Module-3

- Unit-p-Block elements

- Chapter : 17-Group elements.

p-Block elements

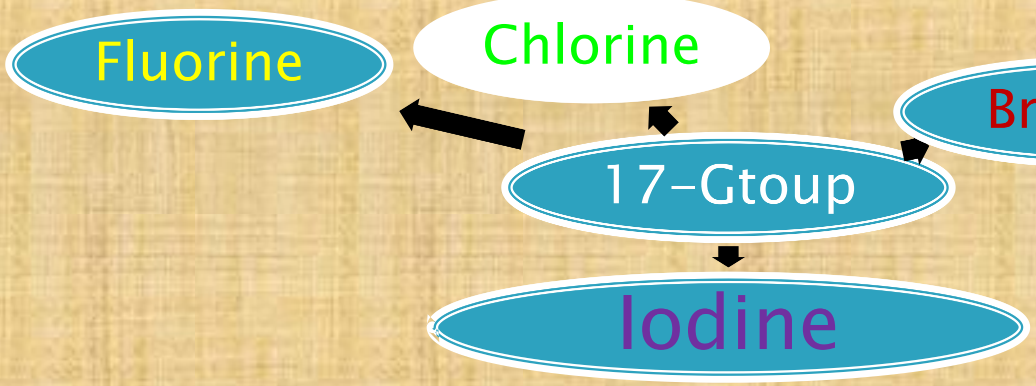
17-Group elements

Syllabus

- Group 17 elements :
- General introduction,
- electronic configuration,
- oxidation states,
- occurrence,
- trends in physical and chemical properties;
- preparation, properties and uses of chlorine and hydrochloric acid.
- Compounds of halogens
- interhalogen compounds,
- oxoacids of halogens (structures only).

Introduction

- This group contains five elements i.e., fluorine, chlorine, bromine, iodine and astatine . They are non-metals and are collectively named as **halogens.** The name halogens meaning sea salt formers.



Fluorine

Chlorine

Bromine

17-Gtoup

Iodine

Electronic configuration

- General electronic configuration : ns^2np^5

OR

$ns^2\ np_x^{\,2}\ \ np_y^{\,2}\ np_z^{\,1}$

This is the elecronic configuration of valency cell. It indicates this is one electron less than nearest noble gas configuration.

Oxidation states

- Fluorine usually shows a negative oxidation state of –1 except in HOF where it shows an oxidation state of +1.

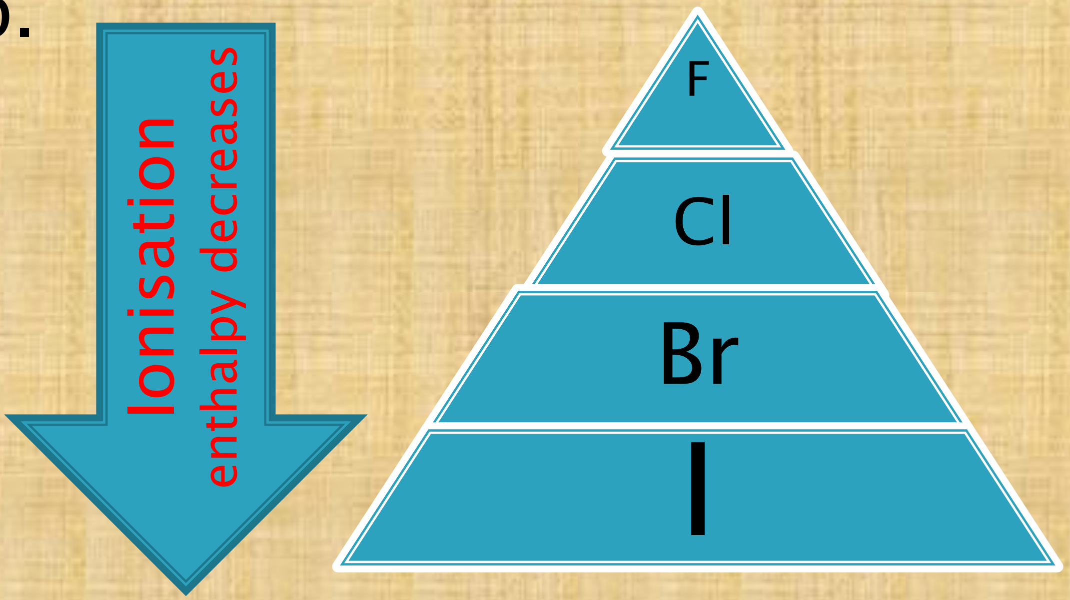
- The other halogens, in addition to a negative oxidation state of –1 also show positive oxidation states +1, +3, +5, +7 .

Occurrence

- Halogens are highly reactive elements and hence do not occur in the free or native state. They mainly occur in the combined state in form of their halide salts.
- Fluorine is present mainly as insoluble fluorides and small quantities are present in soil, river water plants and bones and teeth of animals.
- Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution.
- Chlorine is the most abundant of all the halogens and occurs as chlorides. The chief source of chlorine is sea water, salt wells and salt beds.

Trends in Physical & atomic properties

- (1) Ionisation enthalpy : They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy decreases down the group.



Trends in Physical & atomic properties

- (2)) Electron gain enthalpy : Halogens have large negative electron gain enthalpies, because they have one electron less than the nearest noble gas configuration.
- The negative value decreases down the group.
- The electron gain enthalpy of fluorine is less negative than the chlorine due to its smaller size.

Trends in Physical & atomic properties

- (3) Electronegativity : Halogens are highly electronegative, due to their small size and high nuclear charge. Fluorine is the most electronegative element in periodic table with E.N. value 4.
- The electronegativity decreases down the group.

Trends in Physical & atomic properties

- (4) M.P. and B.P. : All halogens exist as diatomic molecules in the elemental state, these molecules are held together by weak van der Waals forces of attraction. The strength of these forces increases as the size of the halogen increases from fluorine to iodine. As a result, F_2 and Cl_2 are gases at room temperature, Br_2 is a liquid whereas I_2 is solid.
- The M.P and B.P. increases down the group because the forces of attraction increases as the size of halogen increases.

Trends in Physical & atomic properties

(5) Enthalpy of dissociation : On moving down in the group EOD decreases because on moving down the group size of halogen increases, bond length of X–X bond increases, bond strength decreases.

- The bond dissociation enthalpy of fluorine is lower than that of Cl_2 and Br_2 due to its smaller size and hence high electronic repulsion.
- Thus the bond dissociation enthalpy follows the sequence :

$Cl_2 > Br_2 > F_2 > I_2$.

Trends in Physical & atomic properties

(6) Colour : All the halogens are coloured. The colour is due to the fact that their molecules absorb light in the visible region as a result of which their electrons are excited to higher energy levels while the remaining light is transmitted. The colour of halogens is actually the colour of this transmitted light.

- Colour
- Pale yellow (F)
- Greenish yellow (Cl)
- Reddish brown(Br)
- Deep violet(I)

Trends in chemical properties

(1) Reactivity : 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.

Trends in chemical properties

- (2) Oxidising power : Since all the halogens have a strong tendency to accept an electron, they act as strong oxidizing agents. This power decreases down the group. Since F_2 is the strongest oxidizing agent amongst halogens, it will oxidize all the other halide ions to the corresponding halogen in solution or in the dry state.
- $F_2 + 2 X^- \text{----->} 2F^- + X_2$; ($X^- = Cl^-$, Br^- , I^-)
- In general, a halogen of lower atomic number oxidizes halide ions of higher atomic number.

Trends in chemical properties

- (3) Reactivity towards hydrogen: All the halogens combine with hydrogen to form hydrogen halides (HX).

  $H_2 + X_2$ -----------> 2HX
- The reactivity decreases down the group, fluorine combines with hydrogen violently even in dark, chlorine reacts in diffused sunlight, bromine reacts with hydrogen only on heating while iodine reacts with hydrogen in presence of Pt as catalyst. Hydrogen halides dissolve in water to form hydrohalic acids.
- The acidic strength of these acids varies 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.

Chlorine

- Indroduction :
- Chlorine was discovered in 1774 by Scheele by the action of HCl on MnO2.

- In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, *chloros* = greenish yellow).

Chlorine

- Preparation :
- It can be prepared by any one of the following methods:
- (i) By heating manganese dioxide with concentrated hydrochloric acid.

$MnO_2 + 4HCl \text{ --> } MnCl_2 + Cl_2 + 2H_2O$

- However, a mixture of common salt and concentrated H_2SO_4 is used in place of HCl.

$MnO_2 + 4NaCl + 4H_2SO_4 \text{ ---> } MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

- (ii) By the action of HCl on potassium permanganate.

$2KMnO_4 + 16HCl \text{ -->} 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

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Chlorine

- Properties :

(1) It is a greenish yellow gas with pungent and suffocating odour.

- It is about 2-5 times heavier than air. It can be liquefied easily into greenish yellow liquid which boils at 239 K.
- It is soluble in water.

(2) Chlorine reacts with a number of metals and non-metals to form chlorides.

- $2Al + 3Cl_2 \text{-->} 2AlCl_3$; $P_4 + 6Cl_2 \text{--->} 4PCl_3$
- $2Na + Cl_2 \text{--->} 2NaCl$; $S_8 + 4Cl_2 \text{---->} 4S_2Cl_2$
- $2Fe + 3Cl_2 \text{-->} 2FeCl_3$

(3) It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

$H_2S + Cl_2 \text{----->} 2HCl + S$

$C_{10}H_{16} + Cl_2 \text{------->} 16\ HCl + 10C$

(4)) With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.

$8NH_3 + 3Cl_2 \text{-->} 6NH_4Cl + N_2$;

- $NH_3 + 3Cl_2 \text{--->} NCl_3 + 3HCl$

Chlorine

- Properties :

(5) With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

$2NaOH + Cl_2$ -----> $NaCl + NaOCl + H2O$
(cold and dilute)

$6\ NaOH + 3Cl_2$ ---> $5NaCl + NaClO_3 + 3H_2O$
(hot and conc.)

(6) With dry slaked lime it gives bleaching powder.

- $2Ca(OH)_2 + 2Cl_2$ ----> $Ca(OCl)_2 + CaCl_2 + 2H_2O$

(bleaching powder)

Chlorine

Properties :

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

$Cl_2 + H_2O \text{ ---> } 2HCl + O$

(nascent oxygen)

Coloured substance + O --> Colourless substance

Cholorine

Uses :

It is used (i) for bleaching wood pulp (required for the manufacture of paper and rayon), bleaching cotton and textiles,

(ii) in the extraction of gold and platinum

(iii) in the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc.

(iv) in sterilising drinking water and

(v) preparation of poisonous gases such as phosgene ($COCl_2$), tear gas

(CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

Hydrochloric acid (HCl)

Preparation :

Laboratory method :

It is prepared by heating sodium chloride withConc. sulphuric acid.

$NaCl + H_2SO_4$ -->$NaHSO_4 + HCl$

NaHSO4 + NaCl --> $Na_2SO_4 + HCl$

HCl gas can be dried by passing through concentrated sulphuric acid.

Hydrocholoric acid(HCl)

Properties :

(1) It is a colourless and pungent smelling gas. It is easily liquefied to a colourless liquid (b.p.189 K) and freezes to a white crystalline solid (f.p. 159 K).

(2) It is extremely soluble in water and ionises as follows:

$$HCl\ (g) + H_2O\ (l) \text{ ------> } H_3O^+\ (aq) + Cl^-(aq)$$

HCl

Properties :

(3) It reacts with NH_3 and gives white fumes of NH_4Cl.

$NH_3 + HCl$ ----------> NH_4Cl

(4) Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

$Na_2CO_3 + 2HCl$ ---->$2NaCl + H_2O + CO_2$

$NaHCO_3 + HCl$ ----> $NaCl + H_2O + CO_2$

$Na_2SO_3 + 2HCl$ ----> $2NaCl + H_2O + SO_2$

HCl

- Uses :

It is used

(i) in the manufacture of chlorine, NH_4Cl and glucose (from corn starch),

(ii) for extracting glue from bones and purifying bone black,

(iii) in medicine and as a laboratory reagent.

Inter halogen compounds

When two different halogens react with each other, interhalogen compounds are formed.

They can be assigned general compositions as XY , XY_3 , XY_5 and XY_7 where X is halogen of larger size and Y of smaller size and X is more electropositive than Y.

As the ratio between radii of X and Y increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is IF_7 (having maximum number of atoms).

Inter halogen compounds

Peparation :

- All interhalogen compounds are prepared by direct combination between the halogens.
- At different temperature and at different conditions different interhalogen compounds are formed.
- $Cl_2 + F_2 \text{ ----> } 2ClF$ (at 437 K)
- $Cl_2 + 3F_2 \text{ --> } 2\ ClF_3$ (at 573 K)
- $Br_2(l) + 5\ F_2 \text{ --> } 2BrF_5(l)$ (F_2 in excess)
- $I_2(g) + 7\ F_2(g) \text{ -------> } 2IF_7(g)$ (523– 573 K)

Inter halogen compounds

Properties :

(1) These are all covalent molecules and are diamagnetic in nature. They are volatile solids or liquids at 298 K except ClF which is a gas. Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.

(2) Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because X–Y bond in interhalogens is weaker than X–X bond in halogens except F–F bond.

Inter halogen compounds

Properties :

(3) All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XY), halite (when XY_3), halate (when XY_5) and perhalate (when XY_7) anion derived from the larger halogen.

$XY + H_2 O \text{-->} HY + HOX$

(4) Their molecular structures are very interesting which can be explained on the basis of VSEPR theory (The XY_3 compounds have the bent 'T' shape, XY_5 compounds square pyramidal and IF_7 has pentagonal bipyramidal structures.

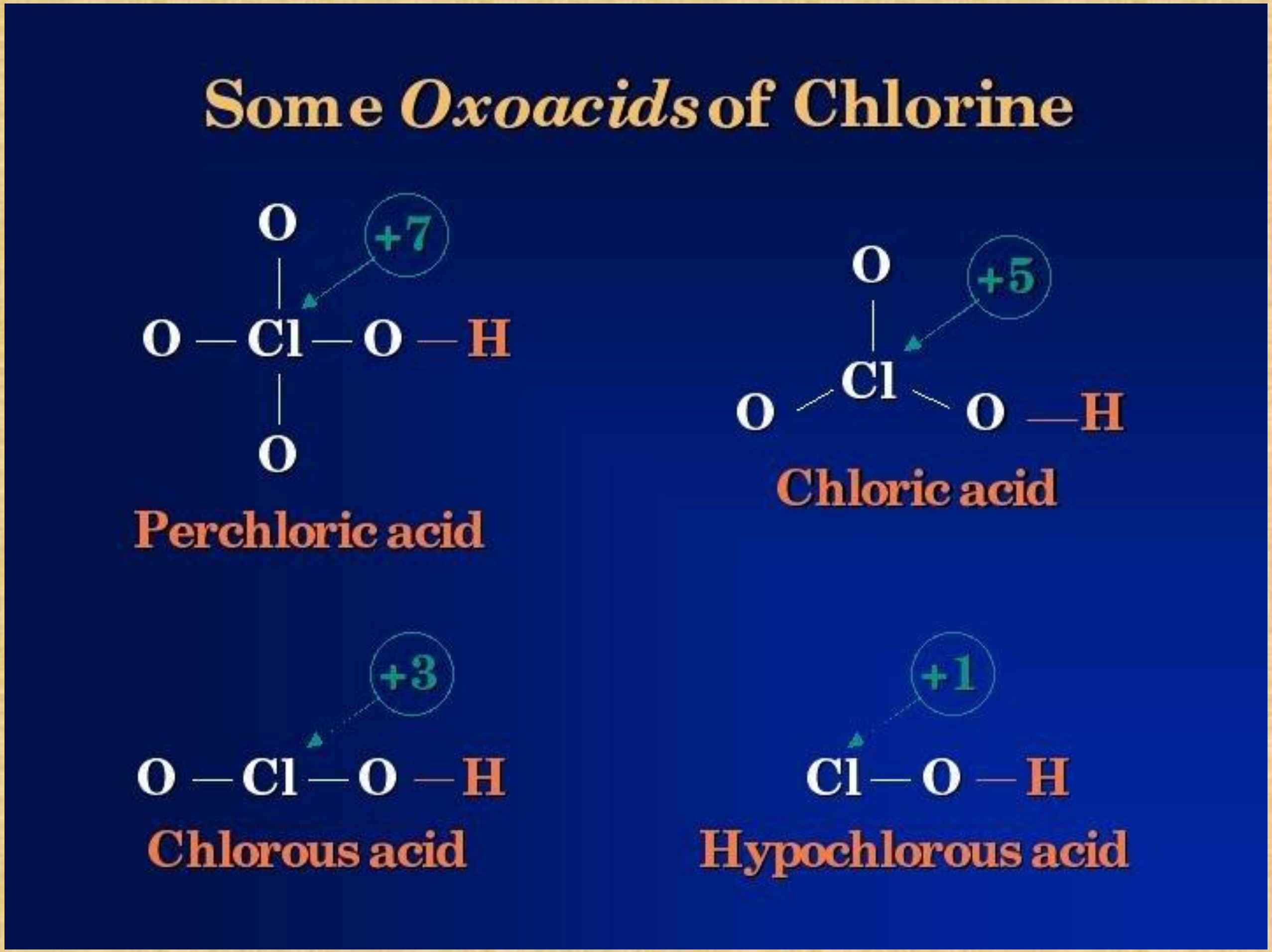
Inter halogen compounds

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.

$U(s) + 3ClF_3(l)$ ------> $UF_6(g) + 3ClF(g)$

Structures of oxoacid of halogens



Some *Oxoacids* of Chlorine

$$\begin{array}{c} O \\ | \\ O-Cl-O-H \\ | \\ O \end{array}$$

Perchloric acid

$$\begin{array}{c} O \\ | \\ O-Cl-O-H \end{array}$$

Chloric acid

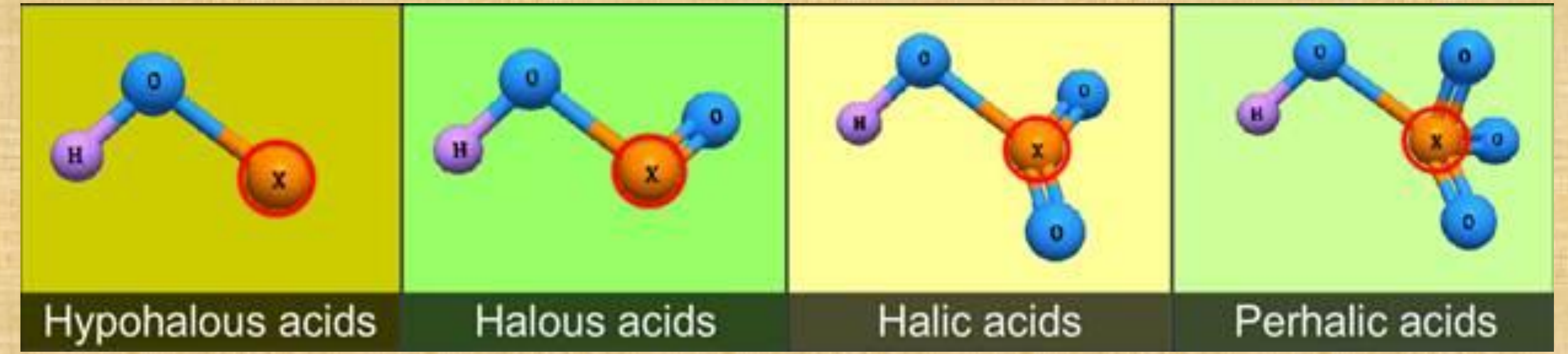
$O-Cl-O-H$

Chlorous acid

$Cl-O-H$

Hypochlorous acid

Structures of oxoacid of halogens



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