CHAPTER / 09

Group 17 Elements: Halogen Family

Topics *Covered*

- Position in the Periodic Table
- General Characteristics of Halogen Family
- Anomalous Behaviour of Fluorine
- Chlorine
- Hydrochloric Acid
- Oxoacids of Halogens
- Interhalogen Compounds
- Pseudohalide Ions and Pseudohalogens

Position in the Periodic Table

Electronic configuration of outer shell of elements of this group is ns^2np^5. As the differentiating electron enters in p-subshell, they are placed in p-block. Due to the presence of seven electrons in outermost shell, the elements are placed in group 17.

Occurrence F, Cl, Br, I and At (astatine) are the elements of group 17. These are collectively known as **halogens** (salt producer). Astatine is a radioactive element and occurs in nature only in traces.

General Characteristics of Halogen Family

Electronic Configuration

All the elements of this group have seven electrons in their outermost shell (ns^2np^5) which is one electron short of the next noble gas.

Some atomic properties of halogens

Elements	Atomic number	Atomic mass	Electronic configuration
Fluorine	9	19	[He] $2s^2\,2p^5$
Chlorine	17	35.45	[Ne] $3s^2\,3p^5$
Bromine	35	80	[Ar] $3d^{10}\,4s^2\,4p^5$
Iodine	53	127	[Kr] $4d^{10}\,5s^2\,5p^5$
Astatine	85	210	[Xe] $4f^{14}\,5d^{10}\,6s^2\,6p^5$

Physical Properties

1. Atomic and Ionic Radii

Atomic and ionic radii of halogens are the smallest in their respective periods due to maximum effective nuclear charge. The atomic radius of F is the smallest among halogens. On moving down the group, atomic and ionic radii increase from F to I due to increase in the number of shells.

2. Ionisation Enthalpy

Halogens have little tendency to lose electron. Thus, they have very high ionisation enthalpy next to inert gas. On moving down the group, ionisation enthalpy decreases due to increase in atomic size.

3. Electron Gain Enthalpy

Halogens have highest negative electron gain enthalpy in their respective periods because they have only one electron less than stable noble gas configuration. Electron gain enthalpy becomes less negative from chlorine to iodine.

4. Electronegativity

Halogens have very high electronegativity. On moving down the group, electronegativity decreases due to increase in atomic size. Fluorine is the most electronegative element in the periodic table.

5. Non-metallic Character

All halogens are typical non-metals and non-metallic character decreases on moving down the group.

6. Colour

Halogens are coloured due to absorption of radiation in visible region which results in excitation of valence shell electrons to higher energy level. They display different colours, e.g. Cl_2 has greenish-yellow, F_2 has yellow, Br_2 has red and I_2 has violet colour.

Chemical Properties

1. Chemical Reactivity

The chemical reactivity of the group 17 elements decreases on going down the group. Fluorine is the most reactive halogen because of low bond dissociation enthalpy, small size and high electronegativity. Halogens react with metals and non-metals to form halides.

2. Oxidation States

All the halogens show –1 oxidation state. Other halogens excluding fluorine show +1, +3, +5 and +7 oxidation states because of gradual promotion of *np*-electrons to *nd*-electrons.

The fluorine atom has no *d*-orbital in its valence shell and therefore cannot expand its octet and hence it shows only –1 oxidation state.

3. Reactivity towards Hydrogen

All halogens react with hydrogen to give hydrogen halides but affinity towards hydrogen decreases down the group. They dissolve in water to produce hydrohalic acids, the acidic strength of these acids increases from HF to HI due to decrease in bond dissociation enthalpy down the group. The stability of these halides decreases down the group, due to decrease in bond (H—X) dissociation enthalpy in the order:

$$\text{H—F} > \text{H—Cl} > \text{H—Br} > \text{H—I}$$

4. Reactivity towards Oxygen

Halogens form many oxides with oxygen but most of the oxides are unstable. Fluorine forms two oxides, i.e. OF_2 and O_2F_2.

5. Reactivity towards Metals

Halogens react with metals to give metallic halides. e.g. bromine reacts with magnesium to give magnesium bromide.

$$\text{Mg}(s) + \text{Br}_2(l) \longrightarrow \text{MgBr}_2(s)$$

The ionic character of metal halides that in decreases down the group. Halides in higher oxidation state are covalent than lower oxidation state, e.g. $SnCl_4$, $PbCl_4$, $SbCl_5$ and UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4, respectively.

6. Reactivity towards Non-metals

A number of non-metals such as *s*, *p*, etc. combine with halogens. The reactivity decreases on moving down the group.

$$\text{S} + 3\text{F}_2 \longrightarrow \text{SF}_6$$
$$\text{S} + 2\text{Cl}_2 \longrightarrow \text{SCl}_4$$

7. Oxidation Action

Halogens are strong oxidising agents. They can potentially oxidise another species and readily accept electrons. Fluorine is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. Fluorine oxidises all the halides.

$$\text{F}_2 + 2X^- \longrightarrow 2\text{F}^- + X_2\,[X = \text{Br, I, Cl}]$$

Bromine oxidises only iodide ion.

$$\text{Br}_2 + 2\text{I}^- \longrightarrow 2\text{Br}^- + \text{I}_2$$

Chlorine oxidises only bromide and iodine ions.

$$\text{Cl}_2 + 2X^- \longrightarrow 2\text{Cl}^- + X_2\,[X = \text{I, Br}]$$

Thus, the oxidising ability of halogens decreases from fluorine to iodine as, $F_2 > Cl_2 > Br_2 > I_2$

8. Reaction with Water

Fluorine oxidises water to oxygen.

$$2\text{F}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4\text{HF}(aq) + \text{O}_2(g)$$

Chlorine and bromine are moderately soluble in water. It gives corresponding hydrohalic and hypohalous acids.

$$X_2(g) + \text{H}_2\text{O}(l) \xrightarrow{\text{Sunlight}} \text{H}X(aq) + \text{HO}X;\,[X = \text{Br or Cl}]$$

Iodine is slightly soluble in water. Iodide ion can be oxidised by oxygen in acidic medium.

$$4I^-(aq) + 4H^+(g) + O_2(aq) \longrightarrow 2I_2(s) + 2H_2O(l)$$

9. Displacement Reactions

Fluorine is the most reactive halogen which displaces all of the other halogen from their salt solutions and is itself displaced by none of the others.

$$F_2 + 2KBr \longrightarrow 2KF + Br_2$$
$$F_2 + 2KI \longrightarrow 2KF + I_2$$

10. Reactivity of Halogens towards Other Halogens

Halogens combine amongst themselves to form interhalogen compounds of the type XX', XX'_3, XX'_5, XX'_7 where, X is a halogen of larger size and X' is a halogen of smaller size.

Anomalous Behaviour of Fluorine

Fluorine is called super halogen as, it differs from other elements of the group because of its exceptionally small atomic and ionic size and low fluorine–fluorine bond dissociation energy. The result of these differences is that, fluorine is the most electronegative element in the periodic table and is a powerful oxidant.

Some of the differences between flourine and other halogens are discussed as follows:

(i) It is more reactive than other halogens because of low F—F bond energy.

(ii) Due to its high electronegativity, the bond between fluorine and other elements is very strong, so its compounds are more stable. Some of them are inert e.g. SF_6.

(iii) Fluorine is almost invariably monocoordinate (CN = 1).

(iv) It always has oxidation state of – 1 (exception HOF) and is never more than monocovalent. It does not show higher oxidation state because of unavailability of *d*-orbitals.

(v) Fluorine is the strongest oxidising agent and oxidises the elements to their highest oxidation state, e.g. in IF_7, iodine has oxidation state of + 7.

(vi) Because of its high electronegativity and small size, fluorine forms strong hydrogen bonds resulting in the properties of hydrogen fluoride being anomalous (at high boiling points), like HF is a liquid and is a weak acid.

Chlorine (Cl_2)

Preparation

Chlorine can be prepared by any one of the following methods :

1. By Oxidation of Hydrochloric Acid

By heating manganese dioxide with conc. HCl.

$$MnO_2 + \underset{\text{(conc.)}}{4HCl} \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

In the above reaction, a mixture of NaCl and conc. H_2SO_4 can be used in place of HCl.

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4\,NaHSO_4 + 2H_2O + Cl_2$$

2. Electrolytic Method

By electrolysis, chlorine is produced from concentrated solution of sodium chloride (brine). It is the commerical method.

$$2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} H_2 + Cl_2 + 2NaOH$$

At anode $2Cl^- \longrightarrow Cl_2 + 2e^-$ (Oxidation)

At cathode $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ (Reduction)

$$2NaCl\text{ (fused)} \xrightarrow{\text{Electrolysis}} 2Na + Cl_2\uparrow$$

3. Laboratory Methods of Preparation

Two methods are used for laboratory preparation of chlorine:

(i) **By the Action of HCl on $KMnO_4$** By the addition of cold conc. HCl to solid $KMnO_4$, Cl_2 is formed.

$$2KMnO_4 + 16HCl \longrightarrow 2MnCl_2 + 2KCl + 8H_2O + 3Cl_2$$

(ii) **By Heating a Mixture of NaCl and MnO_2 with Conc. H_2SO_4**

$$4NaCl + 4H_2SO_4 + MnO_2 \xrightarrow{\Delta} 4NaHSO_4 + MnCl_2 + 2H_2O + Cl_2$$

Manufacture of Chlorine

Chlorine can be manufactured by the following two industrial process:

(i) **Deacon's Process** The Deacon's process has been used as a means of manufacture of chlorine gas. A mixture of hydrochloric acid gas (HCl) and air (O_2) is reacted in the presence of $CuCl_2$ catalyst at 723 K.

$$4HCl + O_2 \xrightarrow[\text{723 K}]{CuCl_2} 2Cl_2 + 2H_2O$$

(ii) **Electrolytic Process** Chlorine can be manufactured by electrolysis of sodium chloride solution (brine). The co-products of chlorine are caustic soda (NaOH) and hydrogen gas (H_2).

The reactions are as follows :

At cathode $2H^+(aq) + 2e^- \longrightarrow H_2(g)$

At anode $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

Overall Process

$$2NaCl + 2H_2O \longrightarrow Cl_2 + H_2 + 2NaOH$$

Physical Properties

(i) It is a greenish-yellow gas with pungent and suffocating odour which is about 2-5 times heavier than air.

(ii) It is highly soluble in water and its aqueous solution is called chlorine water.

(iii) It can be liquefied easily into greenish-yellow liquid which boils at 239 K.

(iv) Chlorine is a highly electronegative element. It is the third highest electronegative element after F and O.

Chemical Properties

(i) **Reaction with Hydrogen** Chlorine reacts with hydrogen and compounds containing hydrogen to form HCl, as it has great affinity for hydrogen.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

(ii) **Reaction with Alkalies** Chlorine reacts with cold and dilute alkalies producing a mixture of chloride and hypochlorite.

$$\underset{\text{(Cold, dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + \underset{\substack{\text{Sodium}\\\text{hypochlorite}}}{NaOCl} + H_2O$$

But with hot and concentrated alkalies, it gives chloride and chlorate.

$$\underset{\text{(Hot, conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + \underset{\substack{\text{Sodium}\\\text{chlorate}}}{NaClO_3} + 3H_2O$$

(iii) **Reaction with Ammonia** Chlorine reacts with NH_3 under two different conditions.

$$\underset{\text{Excess}}{8NH_3} + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

$$NH_3 + \underset{\text{Excess}}{3Cl_2} \longrightarrow NCl_3 + 3HCl$$

(iv) **Reaction with Dry Slaked Lime** Chlorine reacts with dry slaked lime to give bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow \underset{\substack{\text{Bleaching}\\\text{powder}}}{Ca(OCl)_2} + CaCl_2 + 2H_2O$$

(v) **Reaction with Metals and Non-metals** Chlorine reacts with number of metals and non-metals to form chlorides.

$$2Na + Cl_2 \longrightarrow 2NaCl$$
$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

(vi) **Bleaching Property** Chlorine water on standing loses, its yellow colour due to the formation of HCl and HOCl.

$$\begin{array}{l} Cl_2 + H_2O \longrightarrow HCl + HOCl \\ \underline{\quad HOCl \longrightarrow HCl + [O]} \text{ (Nascent oxygen)} \\ Cl_2 + H_2O \longrightarrow 2HCl + [O] \end{array}$$

(vii) **Oxidising Property** It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphur trioxide and iodine to iodate.

(a) It oxidises Fe^{2+} to Fe^{3+}

$$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$$

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

(b) It oxidises SO_3^{2-} to SO_4^{2-}

$$Na_2SO_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + 2HCl$$

(viii) **Addition Reaction** Chlorine adds to unsaturated hydrocarbons to form addition products.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

(ix) **Substitution Reaction** Chlorine forms a number of substitution products with saturated hydrocarbons in the presence of sunlight.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

Uses

(i) For bleaching wood pulp (required for the manufacture of paper and rayon), bleaching cotton and textiles.

(ii) In the manufacturing of dyes, drugs and some organic compounds, like DDT, carbon tetrachloride, refrigerants etc.

(iii) In the preparation of poisonous gases such as, phosgene ($COCl_2$), tear gas (CCl_3NO_2) and mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

(iv) In sterilising drinking water.

(v) In the extraction of gold and platinum.

Hydrochloric Acid (HCl)

Hydrochloric acid is the simplest chlorine based acid system containing water. It is a solution of hydrogen chloride and water, and variety of other chemical species including hydronium and chloride ions.

Preparation of Hydrochloric Acid

It is prepared by heating NaCl with concentrated H_2SO_4.

$$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823\text{ K}} Na_2SO_4 + HCl$$

Physical Properties

(i) It is a colourless and pungent smelling gas.

(ii) It is easily liquefied ($\text{b. p.} = 189\text{K}$) to a colourless liquid and freezes ($\text{f. p.} = 159\text{K}$) to a white crystalline solid.

(iii) It's solution in water is used as a strong acid.

(iv) It attacks mucous membrane on inhalation.

(v) It forms constant boiling point mixture i.e. azeotropes.

Chemical Properties

It is extremely soluble in water and ionises as:

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq); \; K_a = 10^7$$

High value of K_a (dissociation constant) indicates that, it is a strong acid in water.

(i) **Reactions as Reducing Agent** In the presence of strong oxidising agents it acts as a reducing agent and chlorine is formed in all reactions.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

(ii) **Reaction with Fluorine** Fluorine displaces chlorine from HCl, as fluorine is more electronegative than chlorine.

$$2HCl + F_2 \longrightarrow 2HF + Cl_2$$

(iii) **Reaction with Ammonia** It gives white fumes of NH_4Cl on reaction with NH_3.

$$NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl}$$

(iv) **Reaction with Base** It decomposes salts of weaker acids and form corresponding chlorides as:

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

(v) **Acidic Properties** HCl react with most of metals like Zn, Fe, Sn and Na forming metal chlorides and hydrogen gas as by product.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$
$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

(vi) **Action of Salts** It decomposes the salts of weaker acids, such as sulphides, sulphites, nitrites and thiosulphates to give chlorides.

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + S + SO_2$$
$$FeS + 2HCl \longrightarrow FeCl_2 + H_2S$$

(vii) **Formation of *Aqua-regia*** A mixture of three parts of concentrated hydrochloric acid and one part of conc. nitric acid forms *aqua-regia*.

$$\underset{\text{Gold}}{Au(s)} + \underset{\text{Nitrate ion}}{NO_3^-(aq)} + \underset{\text{Hydrogen ion}}{4H^+(aq)} + \underset{\text{Chloride ion}}{4Cl^-(aq)} \longrightarrow$$
$$\underset{\text{Tetra chloroaurate}}{AuCl_4^-(aq)} + NO + \underset{\text{Water}}{2H_2O(l)}$$

(viii) **Precipitation Reaction** HCl reacts with soluble salts of Hg, Pb and Ag to form insoluble chlorides.

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$$

Uses

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

(ii) In medicines and as laboratory reagent.

(iii) For extracting glue from bones and purifying bone black.

(iv) In the preparation of *aqua-regia*.

(v) In the manufacturing of dyes and in textile industries.

Oxoacids of Halogens

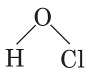
Fluorine forms only one oxoacid HOF, known as **fluoric (I) acid** or **hypofluorous acid** due to high electronegativity and small size.

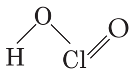
In contrast, chlorine, bromine and iodine form four series of oxoacids. They are stable only in aqueous solutions or in the form of their salts.

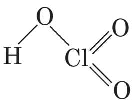
Oxoacids of halogens

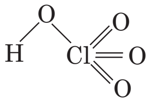
Halic (I) acid (Hypohalous acid)	**HOF** (Hypofluor-ous acid)	**HOCl** (Hypochloro-us acid)	**HOBr** (Hypobrom-ous acid)	**HOI** (Hypoiodous acid)
Halic (III) **acid**	—	HOClO	—	—
(Halous acid)		(Chlorous acid)		
Halic (V) **acid**	—	$HOClO_2$	$HOBrO_2$	$HOIO_2$
(Halic acid)		(Chloric acid)	(Bromic acid)	(Iodic acid)
Halic (VII) **acid**	—	$HOClO_3$	$HOBrO_3$	$HOIO_3$
(Perhalic acid)		(Perchloric acid)	(Perbromic acid)	(Periodic acid)

Structures of Oxoacids of Chlorine


Hypochlorous acid


Chlorous acid


Chloric acid


Perchloric acid

Interhalogen Compounds

Two different halogens may react to form interhalogen compounds as,

$XX' =$ ClF, BrF, BrCl, IF, ICl, etc.

$XX'_3 = ClF_3, BrF_3, IF_3, ICl_3$, etc.

$XX'_5 = ClF_5, BrF_5, IF_5$, etc.

$XX'_7 = IF_7$ (where, X is the halogen of larger size, while X' is the halogen of smaller size.)

Properties of Interhalogen Compounds

All interhalogen compounds are covalent and diamagnetic in nature. ClF is a gas but others are volatile liquids or solids at 298 K. These compounds are more reactive than halogens except fluorine because X—X' bond in interhalogen compounds is weaker than X—X bond in halogens except F—F bond.
All these compounds undergo hydrolysis.

$$XX' + H_2O \longrightarrow \underset{\text{Halide}}{HX'} + \underset{\text{Hypohalite}}{HOX}$$

Some properties of interhalogen compounds

Type	Formula	Physical state and colour	Structure
XX'_1	ClF	Colourless gas	—
	BrF	Pale brown gas	—
	IF(a)	Detected spectroscopically	—
	BrCl(b)	Gas	

	ICl	Ruby red solid (α-form) Brown red solid (β-form)	— —
	IBr	Black solid	—
XX'_3	ClF_3	Colourless gas	Bent T-shaped
	BrF_3	Yellow green liquid	Bent T-shaped
	IF_3	Yellow powder	Bent T-shaped
	ICl_3(c)	Orange solid	Bent T-shaped
XX'_5	IF_5	Colourless gas but solid below 77 K	Square pyramidal
	BrF_5	Colourless liquid	Square pyramidal
	ClF_5	Colourless liquid	Square pyramidal
XX'_7	IF_7	Colourless gas	Pentagonal bipyramidal

where, (a) = Very unstable; (b) = The pure solid is known at room temperature; (c) = Dimerises as Cl-bridged dimer (I_2Cl_6).

Halide ion is always derived from smaller halogen, while hypohalite, halite, halate and perhalate anion is derived from larger halogen.

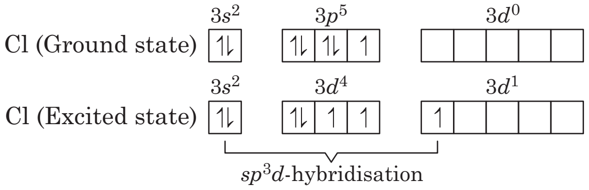
NOTE The molecular structures of interhalogen compounds can be explained on the basis of VSEPR theory.

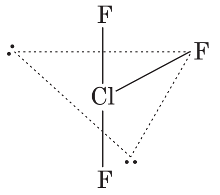
Structure of Interhalogen Compounds

Structure of interhalogen compounds is explained on the basis of VSEPR theory.

(i) ***XX'_3* Type** In these type of compounds, the central atom *X* has sp^3d-hybridisation. It has trigonal bipyramidal shape or T-shape.

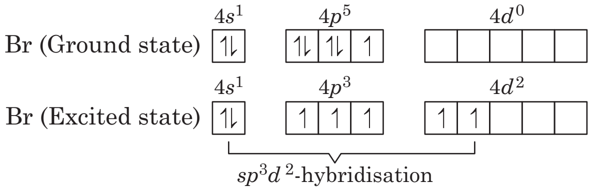
For example - Structure of ClF_3

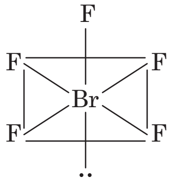




Bent T-shaped geometry

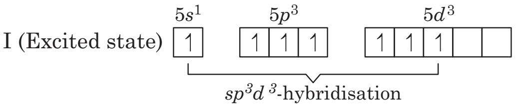
(ii) ***XX'_5* Type** In these type of compounds, the central atom *X* has sp^3d^2-hybridisation. It has distorted octahedral geometry or square pyramidal shape as there are three bond pairs and one lone pair around the central atom. e.g. Structure of BrF_5.

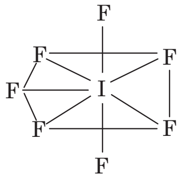




Square pyramidal geometry

(iii) ***XX'_7* Type** In these type of compounds, the central atom *X* has sp^3d^3-hybridisation. It has pentagonal bipyramidal geometry. e.g. Structure or IF_7.





Uses

(i) These are used as fluorinating agents.

(ii) ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$$U(s) + 3ClF_3(l) \longrightarrow UF_6(g) + 3ClF(g)$$

Pseudohalide Ions and Pseudohalogens

The ions that contain two or several uni-negative groups out of which one is nitrogen and which show characteristics of halide ions are called **pseudohalide ions**.

As the halides of pseudohalide ions are called halogens, the covalent dimers of pseudohalide ions are called **pseudohalogens**. Some of them are :

Some Pseudohalides and Pseudohalogens alongwith their Formulae

Pseudohalide ions	Formulae	Pseudohalogens	Formula
Cyanide	CN^-	Cyanogen	$(CN)_2$
Cyanate	OCN^-	Oxocyanogen	$(OCN)_2$
Thiocyanate	SCN^-	Thiocyanogen	$(SCN)_2$
Selenocyanate	$SeCN^-$	Selenocyanogen	$(SeCN)_2$
Azidothiocarbonate	$SCSN_3^-$	Azidocarbon disulphide	$(SCSN)_2$
Isocyanate	ONC^-		

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 What is the action of chlorine with hot and conc. NaOH? **[2019]**

Sol Chlorine reacts with hot and concentrated NaOH to form NaCl and $NaClO_3$.

$6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

Q.2 What happens, when chlorine gas is passed through cold solution of NaOH? **[2019, 2011]**

Sol The reaction is as follows:

$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$

Q.3 Which halogen shows only one oxidation number in its compounds? **[2014]**

Sol Fluorine shows only one oxidation number in its compounds, i.e. –1.

Q.4 In the halogen family, the oxidising action increases in the order. **[2014, 2010, 2008, Textbook]**

(a) $F < Cl < Br < I$ (b) $Cl < I < Br < F$

(c) $I < Br < Cl < F$ (d) $I < Cl < Br < F$

Sol (*c*) In the halogen family, the oxidising property increases in the following order:

$I < Br < Cl < F$

Q.5 Which of the following chemicals liberates bromine from a solution of KBr? **[2013]**

(a) Cl_2 (b) HI (c) I_2 (d) $MgCl_2$

Sol (*a*) Cl_2 displaces bromine from a solution of KBr.

$Cl_2 + 2KBr \longrightarrow 2KCl + Br_2$

Q.6 Why is hydrofluoric acid the weakest of all halogen acids? **[2012, 2009]**

Sol Hydrofluoric acid exists as associated molecules by hydrogen bonding.

Hence, it is the weakest acid of all halogen acids.

Q.7 Which has the highest electron affinity? **[2012]**

(a) Fluorine (b) Chlorine

(c) Bromine (d) Iodine

Sol (*b*) Among halogens, the highest electron affinity is found in chlorine.

Q.8 What happens, when fluorine is passed through concentrated NaOH solution? **[2012 Instant]**

Sol $4NaOH + 2F_2 \longrightarrow 4NaF + 2H_2O + O_2$

Q.9 At room temperature, HCl is a gas, while HF is a liquid. This is because **[2012, 2009]**

(a) H — F bond is covalent

(b) H — F bond is ionic

(c) H — F has metallic bond

(d) H — F has hydrogen bond

Sol (*d*) At room temperature, HF is a liquid due to hydrogen bonding.

Q.10 Why ClF_3 exists, whereas FCl_3 does not exist explain? **[2011]**

Sol F-atom does not have *d*-orbitals and it cannot expand its octet. Therefore, ClF_3 exists, whereas FCl_3 does not exist.

Q.11 Choose the correct order of electron affinity from the following. **[2011, 2006 Instant]**

(a) $F > Cl > Br$ (b) $F < Cl < Br$

(c) $F > Cl < Br$ (d) $F < Cl > Br$

Sol (*d*) The correct order of electron affinity is as follows:

$F < Cl > Br$

Q.12 Which of the following elements does not show positive oxidation state? Oxygen, sulphur, fluorine, chlorine. **[2007]**

Sol **Fluorine** The cause is that, it is the most electronegative element.

Q.13 Which acid is used to draw picture on the glass? **[2005]**

Sol HF is used to draw picture on the glass.

Q.14 What is the role of MnO_2 in the preparation of Cl_2 from HCl? **[2003]**

Sol MnO_2 acts as an oxidising agent.

$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

Q.15 What is the oxidation number of oxygen in OF_2? **[2002]**

Sol Oxygen exhibits + 2 oxidation number in OF_2.

Q.16 Arrange the following in the order of increasing size. Cl, Cl^+, Cl^- **[2001]**

Sol The order of increasing size is

$Cl^+ < Cl < Cl^-$.

Important Questions

Q.17 The electronic configuration of halogen is **[Textbook]**

(a) ns^2 (b) ns^2np^3 (c) ns^2np^5 (d) ns^2np^4

Sol (*c*) The elements of group 17 are called the halogens. The general electronic configuration of halogens is ns^2np^5.

Q.18 Which of the following shows only one oxidation state? **[Textbook]**

(a) F (b) Cl (c) Br (d) I

Sol (*a*) Fluorine is most electronegative element. No any element can take an electron from fluorine, so it has only one oxidation state, i.e. – 1.

Q.19 Most electropositive halogen is **[Textbook]**

(a) F (b) Cl (c) Br (d) I

Sol (*d*) Iodine is the least reactive and the most electropositive halogen. It tends to lose electrons and form positive ions during chemical reactions.

Q.20 The smallest atom is **[Textbook]**

(a) F (b) Cl (c) Br (d) I

Sol (*a*) Due to high electronegativity and presence of lowest number of shells, the first member of the halogen family, i.e. F is the smallest atom.

Q.21 Halogen having highest bond energy. **[Textbook]**

(a) F_2 (b) Cl_2 (c) I_2 (d) Br_2

Sol (*b*) Cl_2 has highest bond energy. The bond energy of fluorine is lower than that of chlorine and bromine as interelectronic repulsion is very high. That's why the correct decreasing order of bond energy is as follows:

$$Cl_2 > Br_2 > F_2 > I_2$$

Q.22 Bleaching powder is **[Textbook]**

(a) $CaClO_3$ (b) CaClO (c) $CaOCl_2$ (d) $Ca(OCl)_2$

Sol (*d*) Calcium hypochlorite $[Ca(OCl)_2]$ is called bleaching powder.

Q.23 Which of the following statement is correct? **[Textbook]**

(a) Br_2 is more reactive than Cl_2
(b) I_2 is more reactive than Br_2
(c) Cl_2 is insoluble in water
(d) Iodine is solid

Sol (*d*) The halogens exist, at room temperature, in all three states of matter, i.e. gases such as fluorine and chlorine, solids such as iodine and liquid as bromine.

Q.24 Sea weeds are important source of **[Textbook]**

(a) Fe (b) I_2 (c) Cl_2 (d) Br_2

Sol (*b*) Sea weeds are important source of iodine (I_2).

Q.25 What is the correct bond energy of the following C—*X* bond (where, *X* = Cl, Br, I)? **[Textbook]**

(a) C—Cl > C—Br > C—I
(b) C—I > C—Cl > C—Br
(c) C—Br > C—Cl > C—I
(d) C—I > C—Br > C—Cl

Sol (*a*) The electronegativity of halogens decreases down the group, whereas the atomic size increases down the group. As the size of halogen atom increases, the C—*X* bond becomes weaker and hence the bond energy of C—*X* bond decreases down the group. Therefore, the correct order of bond energy is,

C— Cl > C—Br > C—I

Q.26 The strongest oxidising element is **[Textbook]**

(a) F (b) Cl (c) Br (d) I

Sol (*a*) Fluorine is the strongest oxidising element.

Q.27 Which of the following has the highest molar heat of vaporisation? **[Textbook]**

(a) HF (b) HCl (c) HBr (d) HI

Sol (*a*) HF has strong intermolecular H-bonding, thus it has the highest molar heat of vaporisation.

Q.28 Which of the following ions can bring about the highest oxidation state of a transition metal? **[Textbook]**

(a) F^- (b) Cl^- (c) Br^- (d) I^-

Sol (*a*) Fluorine is the most electronegative element and it can bring about the highest oxidation state of a transition metal.

Q.29 The halogen that is most readily reduced is **[Textbook]**

(a) chlorine (b) bromine
(c) iodine (d) fluorine

Sol (*d*) The most readily reduced halogen is fluorine. It has the greatest tendency to gain electrons.

Q.30 Which of the following has greatest reducing power? **[Textbook]**

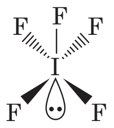
(a) HCl (b) HI (c) HF (d) HBr

Sol (*b*) HI is the strongest reducing agent. It is due to less bond dissociation energy of H—I.

Q.31 Structure of IF_5 is **[Textbook]**

(a) linear
(b) pentagonal bipyramidal
(c) bent T-shaped
(d) square pyramidal

Sol (*d*) Structure of IF_5 is square pyramidal.



Q.32 The compounds used as refrigerants are **[Textbook]**

(a) NH_3 (b) CCl_4
(c) CF_4 (d) CF_2Cl_2
(e) CH_2F_2

Sol (*a,d*) Both NH_3 and CF_2Cl_2 are used refrigerants.

Q.33 Tear gas is **[Textbook]**

(a) $COCl_2$ (b) $CaOCl_2$ (c) NH_3 (d) CCl_3NO_2

Sol (*d*) The compound 2-chlorobenzalmalononitrile is called tear gas. It's general chemical formula is CCl_3NO_2.

Q.34 Which of the following is used for the preparation of fluorine?

(a) Only KHF_2 (b) Only OF_2

(c) Both O_2 and OF_2 (d) Either O_2 or OF_2

Sol (*a*) Only KHF_2 can be used for the preparation of fluorine.

Q.35 Give the reason for bleaching action of Cl_2.

Sol Bleaching action of Cl_2 is due to its oxidising property.

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

$$\text{Coloured substance} + O \longrightarrow \text{Colourless substance}$$

2 MARK *Questions*

Exams' Questions

Q.36 What happens when chlorine gas is passed through cold solution of NaOH? **[2019, 2011]**

Sol When chlorine gas is passed through cold solution of NaOH, then sodium chloride and sodium hypochlorite are formed.

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$ **(2)**

Q.37 HF is a liquid, whereas HCl is a gas. Explain. **[2018, 2013, 2004]**

Sol HF shows the property of intermolecular hydrogen bonding and exists as associated molecules. Hence, HF is a liquid. On the other hand, HCl exists as isolated molecules as, it does not exhibit hydrogen bonding. **(2)**

Q.38 Why hydrogen bromide cannot be prepared by reacting sodium bromide with concentrated H_2SO_4? **[2015]**

Sol It is because the HBr formed in the reaction is a reducing agent and reduces H_2SO_4 to SO_2. The reaction is as follows:

$$[NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr] \times 2$$

$$H_2SO_4 + 2HBr \longrightarrow 2H_2O + SO_2 + Br_2$$ **(2)**

Q.39 Explain, what happens when HCl gas is passed through concentrated NaCl solution? **[2013, 2003, Textbook]**

Sol When HCl gas is passed through concentrated NaCl solution, then NaCl gets precipitated due to common ion effect. It is the method for the purification of NaCl. **(2)**

Q.40 Why HF cannot be stored in glass bottles? Explain with equations. **[2012, 2006]**

Sol HF causes etching of glass. Hence, it cannot be stored in glass bottles. **(1)**

$$\begin{array}{l} Na_2SiO_3 + 6HF \longrightarrow 2NaF + SiF_4 + 3H_2O \\ SiF_4 + 2HF \longrightarrow H_2SiF_6 \\ \hline Na_2SiO_3 + 8HF \longrightarrow 2NaF + H_2SiF_6 + 3H_2O \end{array}$$ **(1)**

Q.41 How does the bleaching action of chlorine differ from that of sulphur dioxide? Explain. **[2010, 2009, 2008]**

Sol The bleaching action of chlorine is permanent because of oxidation, but that of SO_2 is temporary because of reduction. **(2)**

Q.42 What happens when potassium bromide is treated with concentrated sulphuric acid? **[2007]**

Sol When potassium bromide is treated with conc. H_2SO_4, then Br_2 is formed.

$$2KBr + 3H_2SO_4 \longrightarrow 2KHSO_4 + SO_2 + Br_2 + 2H_2O$$ **(2)**

Q.43 Give two examples and two general characteristics of interhalogen compounds. **[2006]**

Sol ClF and BrF are interhalogen compounds. They are covalent and diamagnetic in nature. **(2)**

Q.44 Why hydroiodic acid cannot be prepared by reacting KI with concentrated H_2SO_4? **[2006]**

Sol Hydroiodic acid (HI) cannot be prepared by reacting KI with concentrated H_2SO_4, because the HI formed get oxidised to iodine. **(2)**

Q.45 How do the following pair of compounds react with each other? KBr and concentrated H_2SO_4. **[2006]**

Sol KBr reacts with concentrated H_2SO_4 to form Br_2 gas. The reaction is as follows: **(1)**

$$2KBr + 3H_2SO_4 \longrightarrow 2KHSO_4 + SO_2 + Br_2 + 2H_2O$$ **(1)**

Q.46 HF is less volatile than HCl. Explain. **[2003]**

Sol HF is less volatile as, it exists as associated molecules due to extensive hydrogen bonding, while HCl does not have extensive hydrogen bonding. **(2)**

Important Questions

Q.47 What happens when NaCl is heated with $K_2Cr_2O_7$ and conc. H_2SO_4? **[Textbook]**

Sol When NaCl is heated with $K_2Cr_2O_7$ and conc. H_2SO_4, Cl_2 gas is produced as shown below:

$$6NaCl + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Cl_2\uparrow + Cr_2(SO_4)_3 + 3Na_2SO_4 + K_2SO_4 + 7H_2O$$ **(2)**

Q.48 Write the balanced equations for the following:

(i) NaCl is heated with sulphuric acid in the presence of MnO_2.

(ii) Chlorine gas is passed into a solution of NaI in water.

Sol (i) $4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + Cl_2 + 2H_2O$ **(1)**

(ii) $2NaI + Cl_2 \longrightarrow 2NaCl + I_2$ **(1)**

Q.49 Write the reaction of F_2 and Cl_2 with water.

Sol Fluorine reacts with H_2O to produce O_2 and ozone.

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

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$ **(1)**

Chlorine reacts with water in the presence of sunlight to produce nascent oxygen.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$ **(1)**

3 MARK *Questions*

Exams' Questions

Q.50 Arrange the following in the order of property indicated for each set. **[2016]**

(i) F_2, Cl_2, Br_2, I_2 increasing bond dissociation enthalpy.

(ii) HF, HCl, HBr, HI increasing acid strength.

(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_2 increasing base strength.

Sol (i) The bond dissociation enthalpy of fluorine is lower than those of chlorine and bromine because the interelectronic replusion is very high. So, the order $I_2 < F_2 < Br_2 < Cl_2$ is the correct order of increasing bond dissociation enthalpy. **(1)**

(ii) All the halogen acids ionise to give H^+ ion and halide ion X^- (where, $X^- = F^-, Cl^-, Br^-, I^-$). The bond in HI is weaker than those in HF, HCl and HBr, therefore HI is the strongest acid.
$HF < HCl < HBr < HI$ increasing acid strength. **(1)**

(iii) The size of a central atom of nitrogen is smaller than other given compounds and this property increases its basicity. Therefore, the correct order of increasing base strength is as follows:

$$BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$$ **(1)**

Q.51 What are inter halogen compounds? Give two examples of these compounds. **[2015]**

Sol When two different halogens form a binary compound, it is known as interhalogen compound. Such compounds are formed due to the difference in the electronegativities of halogen atoms. The general formula of interhalogen compound is AX_n, where A is always bigger and X is smaller halogen atom and $n = 1, 3, 5$ or 7. They are covalent in nature. The maximum value of n for iodine is 7, bromine is 5 and chlorine is 3. Interhalogen compounds may be of the following types:

AX type : ClF, ICl, AX_3 type : ClF_3, BrF_3

AX_5 type : IF_5, BrF_5, AX_7 type : IF_7 **(3)**

Q.52 Explain, why fluorine exhibits an oxidation state of −1 only, while other elements of the family exhibit oxidation states of −1, +1, +3, +5 and +7? **[2013]**

Sol Due to its highest electronegativity, flourine exihibits an oxidation state (−1) and does not show any positive oxidation state. It does not exhibit higher oxidation states (+ ve or −ve) due to the absence of vacant *d*-orbitals. While, other members, shows oxidation state of −1, + 1, + 3, +5 and +7. **(3)**

Important Questions

Q.53 (i) Why are interhalogen compounds more reactive than its elemental form?

(ii) Why are special methods used to prepare HBr and HI?

Sol (i) Since, $X—X'$ bond between two different electronegative elements is weaker than that of two same elements, thus interhalogen compounds have low bond dissociation enthalpy and are more reactive. **(1½)**

(ii) HBr and HI being moderate reducing agents, reduce H_2SO_4 used for the preparation of HBr and HI to SO_2 and themselves get oxidised to Br_2 and I_2 respectively. Thus, special methods are used to prepare HBr and HI. **(1½)**

7 MARK *Questions*

Exams' Questions

Q.54 Describe how chlorine gas is prepared in the laboratory without heating. How does chlorine react with (*a*) excess of ammonia and (*b*) hot sodium hydroxide solution? Explain with equation. **[2011, 2006]**

Sol **Preparation of Chlorine** Chlorine can be prepared by heating manganese dioxide with conc. HCl.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

Important Points In the reaction, a mixture of NaCl and conc. H_2SO_4 can be used in place of HCl.

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

It can also be obtained by the action of HCl on potassium permanganate.

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Manufacture of Chlorine Chlorine can be manufactured by the following two processes

(i) **Deacon's Process** It can be manufactured by Deacon's process in which oxidation of HCl gas is done by atmospheric O_2 in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4HCl + O_2 \xrightarrow[723\ K]{CuCl_2} 2Cl_2 + 2H_2O$$

(ii) **Electrolytic Process** Chlorine can be obtained by the electrolysis of concentrated solution of NaCl (brine).

$$2NaCl + 2H_2O \longrightarrow 2NaOH + \underset{\text{(At anode)}}{Cl_2(g)} + \underset{\text{(At anode)}}{H_2(g)}$$ **(5)**

(a) Chlorine gives nitrogen and ammonium chloride with excess ammonia.

$$\underset{\text{(Excess)}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$ **(1)**

(b) Chlorine reacts with hot sodium hydroxide solution in the following manner.

$$\underset{\text{(Hot and conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + \underset{\text{Sodium chlorate}}{NaClO_3} + 3H_2O$$ **(1)**

Q.55 Give a comparative account of group VIIA elements (halogen family) of periodic table.
[2003, 2001, Textbook]

Sol Refer to the text of pages 151 and 152. **(7)**

Important Questions

Q.56 Assign reasons for the following.

(i) In liquid state, hydrogen chloride is a stronger acid than hydrogen fluoride.

(ii) Complete the reactions.

(a) $I_2 + HNO_3\,(\text{conc.}) \longrightarrow$

(b) $\underset{\text{(Cold and dilute)}}{NaOH} + Cl_2 \longrightarrow$

(iii) How would you account for the following?

(a) The electron gain enthalpy with negative sign for fluorine is less than that of chlorine, still fluorine is a stronger oxidising agent than chlorine.

(b) Fluorine never acts as the central atom in polyatomic interhalogen compounds.

Sol (i) In liquid state, HCl is a stronger acid than HF, because with increase in H—*X* bond length, bond dissociation energy decreases. **(1)**

(ii) (a) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$ **(1)**

(b) $2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$ **(1)**

(iii) (a) Due to small size of fluorine, it has very high interelectronic repulsions in the 2*p*-orbitals. Hence, incoming electron experiences less attraction from the nucleus and results in high hydration enthalpy of F^-. **(2)**

Therefore, fluorine is a stronger oxidising agent than chlorine.

(b) Fluorine never acts as the central atom in polyatomic interhalogen compounds, since it is the most electronegative element of the group. **(2)**

Q.57 (i) Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of F_2 and Cl_2.

(ii) Why are halogens coloured?

Sol (i) Comparing F_2 and Cl_2 with the given parameters.

(Unit = kJ mol^{-1})	$\Delta_{\textbf{bond diss}}\boldsymbol{H}$	$\Delta_{\textbf{elec gain}}\boldsymbol{H}$	$\Delta_{\textbf{hydr}}\boldsymbol{H}$
F_2	158.8	−333	515
Cl_2	242.6	−349	381

From the data given above, it is clear that the bond dissociation enthalpy and electron gain enthalpy are higher for chlorine but hydration energy is much higher for fluorine.
It compensates the effect of other two and thus makes fluorine more oxidising than chlorine.

$$\frac{1}{2}X_2(g) \xrightarrow{1/2\,\Delta_{\text{diss}}H^\circ} X(g)$$

$$\xrightarrow{\Delta_{eg}H^\circ} X^-(g) \xrightarrow{\Delta_{\text{hyd}}H^\circ} X^-(aq)$$ **(3)**

The relative oxidising power of the halogens can be further illustrated by their reactions with water.

$$2F_2(g) + 2H_2O\,(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$Cl_2(g) + H_2O\,(l) \longrightarrow HCl\,(aq) + HOCl\,(aq)$$ **(2)**

(ii) The colour of halogens is due to the absorption of light in the visible region. As a result, electrons get excited to higher energy level and the compound exhibits colour. **(2)**

Chapter Test

1 MARK Questions

1 The element present in combined state in Laminaria stenophylla is **[Textbook]**

(a) bromine (b) iodine
(c) fluorine (d) chlorine

2 Which of the following displaces Br_2 from an aqueous solution containing bromide ion? **[Textbook]**

(a) Cl_2 (b) Cl^- (c) I_2 (d) I_3^-

3 Which of the following compounds exists? **[Textbook]**

(a) $KHCl_2$ (b) KHF_2 (c) $KHBr_2$ (d) KHI_2

4 The number of electrons in a halogen in its outermost orbit in comparison with corresponding noble gas is **[Textbook]**

(a) one electron less (b) one electron more
(c) two electrons less (d) two electrons more

[***Ans***. 1. (b) 2. (a) 3. (b) 4. (a).]

5 The least volatile hydrogen halide is …… .

[***Ans***. HF]

6 Chemical properties of astatine in comparison with other halogens is known very little to us. Why?

2 MARK Questions

7 Glass apparatus are not used for isolation and storage of fluorine. Why? **[Textbook]**

8 Why is the boiling point of hydrofluoric acid abnormally high? **[Textbook]**

9 ClF_3 molecule is T-shaped in structure and not a trigonal planar one. Explain. **[Textbook]**

10 What happens when chlorine water is added to potassium iodide solution in small quantity? Given equation. **[Textbook]**

11 Why hydrogen fluoride is a liquid, whereas other hydrogen halides are gases? **[Textbook]**

12 Electron affinity of fluorine is less than that of chlorine, why? **[Textbook]**

3 MARK Questions

13 Complete the following reactions:

(i) $NaCl + MnO_2 + H_2SO_4 \longrightarrow$
(ii) $Na_2SO_3 + 2HCl \longrightarrow$
(iii) $Cl + ClF_3$

14 What happens, when Cl_2 reacts with hot conc. NaOH? Show with equation that, this is a disproportionation reaction. **[Textbook]**

15 Why are halogens strong oxidising agents? Name the strongest oxidising halogen. **[Textbook]**

16 Explain, why fluorine forms only one oxo-acid HOF? **[Textbook]**

17 Give the reasons for anomalous behaviour of fluorine. **[Textbook]**

7 MARK Questions

18 Explain the reason as to why inspite of having same electronegativity, nitrogen forms hydrogen bond, whereas chlorine does not?

(i) What are interhalogen compounds? Write some of their properties.
(ii) Why Cl_2 acts as bleaching agent?

19 What happens when the following reactions take place? Write equations. **[Textbook]**

(i) Dry slaked lime reacts with Cl_2.
(ii) NH_3 reacts with excess Cl_2.

20 Write notes on hydrides of halogens. **[Textbook]**