

# 3 CHAPTER



## GROUP 17 ELEMENTS

- \* General Characteristics
- \* Hydrochloric Acid
- \* Chemistry of Chlorine
- \* Oxyacids of Chlorine

### GENERAL CHARACTERISTICS

#### 3.1.1 Position in periodic table

Fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are the five elements of group VIIA. They are located in the p-block of the long form of the periodic table. These elements are assigned group 17 by the I.U.P.A.C. These are called halogens as their salts are formed in sea water. Halogen a Greek word meaning a sea salt.

Their position of these elements in the long form of the periodic table is indicated by shaded portion in Table 3.1.

Table 3.1 Position of group VIIA elements

IA																	0
	IIA											IIIA	IVA	VA	VIA	VIIA	He
															O	F	Ne
															S	Cl	Ar
		IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB				Se	Br	Kr
															Te	I	Xe
															Po	At	Rn

General electronic  
configuration of  
halogens is  $ns^2np^5$

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Each of the group VIIA elements has seven electrons in the valence shell. Two electrons are filled in the s sub-shell and the remaining five in the p sub-shell. The general outer electronic configuration of these elements is  $ns^2np^5$ . Configuration of these elements is summarised in Table 3.2.

The similarities in the properties of elements result very largely from their similar electronic configuration. Only two electrons are present in the penultimate shell of fluorine, eight electrons in chlorine and eighteen electrons each in bromine, iodine and astatine. This shows why fluorine differs in some of its properties from chlorine and these two elements differ in their properties from the remaining elements of the group.



Table 3.2 Atomic numbers and electronic configuration of the group VIIA elements

Element	Symbol	Atomic number	Configuration
Fluorine	F	9	[He] $2s^2 2p^5$
Chlorine	Cl	17	[Ne] $3s^2 3p^5$
Bromine	Br	35	[Ar] $3d^{10} 4s^2 4p^5$
Iodine	I	53	[Kr] $4d^{10} 5s^2 5p^5$
Astatine	At	85	[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$

## 3.1.2

## Occurrence

*Common natural form of halogen is halide. Most available halide is chloride*

Halogens are not available in free state. They are naturally available in combined state, due to their high reactivity. The common natural form of the halogen is halide. Sea is a potential source of halides. Fluorine is less available in sea water, only to the extent of few ppm. Most available halide in sea water is chloride. Sea water contains about 2.5% (w/v) sodium chloride. Solid deposits of sodium chloride on rocks is called rock salt. Bromine is available as  $MgBr_2$  and iodine as  $NaIO_3$ . Chile salt petre contains about 0.2% sodium iodate.

Chlorine and bromine are extracted from brine solution, which is concentrated sea water. The ash of sea weeds is rich with iodide and iodine is extracted from this.

## Important fluoride minerals

Fluorspar :  $CaF_2$   
 Cryolite :  $Na_3AlF_6$   
 Fluorapatite :  $3Ca_3(PO_4)_2 \cdot CaF_2$

## Important chloride minerals

Carnallite :  $KCl \cdot MgCl_2 \cdot 6H_2O$   
 Sylvine :  $KCl$   
 Rock salt :  $NaCl$

The similarities and gradation in the general physical properties of four available halogens are summarised in Table 3.3.

Table 3.3 Gradation in the physical constants of halogens

Property	Fluorine	Chlorine	Bromine	Iodine
Atomic weight	19	34.5	79.9	126.9
Covalent radius ( $A^0$ )	0.65	0.99	1.14	1.33
Ionic radius of $X^-$ ( $A^0$ )	1.33	1.84	1.96	2.20
Melting point ( $^0C$ )	-219	-101	-7	114
Boiling point ( $^0C$ )	-188	-34	60	185
Density ( $g\ cc^{-1}$ )	1.5	1.7	3.2	4.9
Electronegativity (Pauling scale)	4.0	3.0	2.8	2.5
Electron affinity ( $kJ\ mol^{-1}$ )	-333	-349	-325	-296
Ionisation potential ( $kJ\ mol^{-1}$ )	1681	1256	1143	1009
X-X bond energy ( $kJ\ mol^{-1}$ )	158	243	192	152
S.R.P Values	2.85 V	1.36 V	1.09 V	0.54 V
Common oxidation state	-1	-1, +1, +3, +4, +5, +6, +7	-1, +1, +3, +4, +5, +7	-1, +1, +3, +5



### 3.1.3 General properties

*Bromine is the  
only non-metallic  
liquid at 25°C*

*Most electro-  
negative element  
is fluorine*

*Electron affinity  
is highest for  
chlorine*

**Atomic radius :** From fluorine to iodine, the atomic number and the atomic weight gradually increase. The differentiating electron enters in the next higher energy shell, suggesting an increase in the atomic radius. However, the increase in the radius is less predominant beyond chlorine. This is due to the screening effect by the presence of inner d-electrons.

The radius of the halide ions is much larger than the covalent radius of the corresponding halogens. Larger radius of the anion is attributed to a less effective nuclear charge of anion than that of the parent atom. The radius of the halide ions increase gradually from fluoride to iodide.

**Physical state :** The tendency to form condensed molecules increases with increase in atomic number and size. Fluorine and chlorine are gases. Bromine is the only non-metallic liquid at room temperature. Iodine is a volatile solid and can be sublimed.

Halogens exist as diatomic covalent molecules. The van der Waals forces are present between their molecules. The halogens are volatile on account of weak intermolecular forces. With an increase in the size and number of electrons, these forces increase from fluorine to iodine and the molecules are more condensed. Thus bromine is a liquid and iodine is a solid.

**Electronegativity :** The halogens have high values of electronegativity. Fluorine is the most electronegative element and the best non-metal. The electronegativity values decrease from fluorine to iodine. As a result of the decrease of electronegativity, the non-metallic nature decreases down in the group. All halogens are non-metals. However, iodine shows some metallic character in few cases.

**Electron affinity :** Electron affinity values of halogens are high. The element with highest electron affinity is chlorine. The low value of electron affinity of fluorine than that of chlorine is attributed to the small size of fluorine atom. Fluorine has high electron density which makes the addition of electron relatively more difficult.

**Ionisation potential :** Ionisation potential values of halogens are very high among representative elements. Therefore, they have little tendency to form cation,  $X^+$ . The ionisation potential values decrease gradually from fluorine to iodine, suggesting the tendency to form cation increases to iodine. Molten iodine monochloride (ICI) and molten iodine cyanide (ICN) conduct electricity, showing the existence of  $I^+$  cation.

**Colour :** Halogens are all coloured. The reason for the colours exhibited by halogens is absorption of energy in the visible region. The colours of halogens are listed in Table 3.4.

Table 3.4 Colours exhibited by halogens

Halogen	Formula	Bond length	Colour
Fluorine	$F_2$	1.44 Å	Pale yellow
Chlorine	$Cl_2$	1.98 Å	Greenish yellow
Bromine	$Br_2$	2.28 Å	Red
Iodine	$I_2$	2.66 Å	Violet

Halogens absorb the visible radiation and consequently their electrons are excited. The energy for excitation depends upon the size of halogen molecule.



Fluorine is smallest in size among halogens. It requires high energy for excitation. It absorbs high energy violet-indigo radiation and hence appears yellow. On the other hand, iodine is larger in size. It requires relatively less energy for excitation. It absorbs, low energy orange-red radiation and hence appears violet.

Due to lack of vacant valence d-orbitals fluorine cannot expand its valency beyond 1

Bond energies are in the order:  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$

Fluorine has universal oxidation state of -1 in all its compounds

**Bonding and valency :** Each of the halogen element has seven valence electrons and require one more for attaining stable octet configuration. Thus the usual valency of halogens is 1. The maximum valency, however, is the group number 7.

Fluorine is always monovalent in its compounds. It cannot expand its valency greater than 1. This is due to lack of valence d-orbitals in fluorine.

Halogens are covalent and the atomicity of their molecules is 2. One electron pair is shared between atoms of a halogen molecule to form a sigma bond. Bond dissociation energy is highest for chlorine among halogens. Bond energy decreases from chlorine to iodine gradually. Bond dissociation energy of fluorine is less than that of chlorine or bromine. The decreasing order of bond energies of halogens is :  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$ . The exceptionally lower bond energy of fluorine is explained as follows.

Fluorine atom is very small. The internuclear distance in fluorine is only  $1.44 \text{ \AA}$ . Fluorine has notoriously weak bond. This was explained successfully by Coulson. The non-bonding electron pairs of adjacent fluorine atoms in  $\text{F}_2$  molecule are very close to each other. These lone pairs of electrons are under strong repulsion forces. Hence the bond strength in fluorine is reduced.

Earlier Mulliken explained that fluorine has no d-orbitals and hence multiple bonds are not possible in fluorine molecule. But Coulson's explanation is simpler and is widely accepted.

The decrease in the bond energy from chlorine to iodine is attributed to the higher internuclear distances.

**Oxidation numbers :** The general oxidation numbers of the group VIIA elements are -1, +1, +3, +5 and +7. States of +4 and +6 occur in oxides and oxyacids of chlorine and bromine. The element that never exhibits positive oxidation numbers is fluorine. In all its compounds, fluorine has the universal oxidation number, -1.

The oxidation numbers of chlorine are usually odd numbers. Chlorine has one unpaired electron in its ground state as shown in Fig 3.1.

Configuration in ground state	$3s^2$ 	$3p^5$ 	$3d^0$ 
Configuration in first excited state	$3s^2$ 	$3p^4$ 	$3d^1$ 
Configuration in second excited state	$3s^2$ 	$3p^3$ 	$3d^2$ 
Configuration in third excited state	$3s^1$ 	$3p^3$ 	$3d^3$ 

Fig 3.1 Electronic configurations of chlorine



In its ground state, halogen forms only one bond. In its first excited state, halogen usually undergoes  $sp^3d$  hybridisation. Out of five hybridised orbitals two are occupied by lone pairs and the remaining three are useful for bonding. In its second excited state, halogen usually undergoes  $sp^3d^2$  hybridisation. Out of six hybridised orbitals one is occupied by lone pair and the remaining five are useful for bonding. In its third excited state, halogen usually undergoes  $sp^3d^3$  hybridisation. All the seven hybridised orbitals are used for bonding.

## 3.1.4

## Chemical properties

*Fluorine is the most reactive element*

*Reactivity of halogens gradually decreases from fluorine to iodine*

Fluorine is the most reactive of all elements in the periodic table. It reacts with all the other elements except the lighter noble gases helium and neon. It reacts with xenon under mild conditions to form xenon fluorides. Reactions of fluorine with many elements are vigorous and explosive. In the massive form a few metals such as copper, nickel, iron and aluminium acquire a protective fluoride layer and become passive to fluorine.

Halogen atoms have seven electrons in the valence state. They acquire one more electron to form stable octet. The ability of attracting the electron is high for halogens. Hence they are very reactive. Their reactivity, compared to other non-metals, is high due to low dissociation enthalpies of halogens. The reactivity of halogens gradually decrease from fluorine to iodine.

**With hydrogen :** The trend in the reactivity of halogens is evidenced in the reaction with hydrogen. Fluorine reacts with hydrogen even in dark. Chlorine reacts with hydrogen in the presence of diffused light. Bromine reacts with hydrogen upon heating and the reaction is complete in the presence of a catalyst, like platinum. Iodine reacts with hydrogen upon heating and the reaction is never complete since a reversible equilibrium is established. The reaction of halogens with hydrogen and characteristics of hydrogen halides are listed in Table 3.5.

Table 3.5 Preparation and characteristic properties of hydrogen halides

Property	Hydrogen fluoride	Hydrogen chloride	Hydrogen bromide	Hydrogen iodide
Condition of the on reaction	Reaction occurs even in dark light	Reaction is slow in dark, but fast in with Pt catalyst	Reaction occurs on heating at 590 K	Reaction occurs heating at 710 K,
H-X bond length, $\text{\AA}^0$	0.92	1.27	1.41	1.61
H-X bond energy, $\text{kJ mol}^{-1}$	574	433	362	295
Melting point	190 K	159 K	185 K	222 K
Boiling point,	293 K	189 K	206 K	238 K
Thermal stability	Highly stable	Stable	Dissociates on heating	Less stable
pKa value	3.2	-7.0	-9.4	-10.0
Reduction ability	Not a reducing agent	Acts as a reductant and oxidises to chlorine	Stronger reductant and oxidises to bromine	Strongest reductant of all hydrogen halides



Hydrogen fluoride is stable and is a weak acid

Fluorine can oxidise water to oxygen

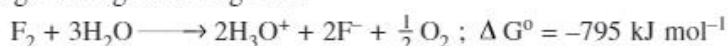
Higher oxides of halogens are more stable

Hydrogen halides are gases. Hydrogen fluoride can be liquified easily. Boiling point of hydrogen fluoride is higher than that of other hydrogen halides. This is because of intermolecular hydrogen bonding in hydrogen fluoride. Most volatile hydrogen halide is hydrogen chloride.

Hydrogen fluoride is the most stable hydrogen halide. Stability of hydrogen halides is in the order :  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$ . In aqueous solutions, HF is a weak acid.

HF attacks silica with the formation of hydrofluoro silicic acid. Other hydrohalic acids are strong acids. Hydrogen halides are good reducing agents. While the oxidation ability decreases from fluorine to iodine, the reduction ability increases from hydrogen fluoride to hydrogen iodide.

**With water :** Halogens are all covalent. They are all soluble in water, but the extent to which they react with water and the reaction mechanism that is followed, vary among halogens. Fluorine is so strong as an oxidant that it oxidises water to oxygen. The reaction is strongly exothermic and spontaneous. The free energy change is large and negative.



Similar reaction with other halogens is possible, but the reaction is slow because of high activation energies. An alternative disproportionation reaction occurs with other halogens.



Bromine is the most soluble halogen in water. The reaction of iodine with water is non-spontaneous, since the free energy change for the reaction is positive. Iodine is more soluble in 10% aqueous potassium iodide solution. This is due to the formation of a complex tri-iodide ion ( $\text{I}_3^-$ ). Ions like  $\text{I}_3^-$ ,  $\text{IBr}_2^-$ ,  $\text{ICl}_4^-$ , etc., are called polyhalides.

**With oxygen :** Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides  $\text{OF}_2$  and  $\text{O}_2\text{F}_2$ . However, only  $\text{OF}_2$  is thermally stable at 298K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.  $\text{O}_2\text{F}_2$  oxidises plutonium to  $\text{PuF}_6$  and the reaction is used in removing plutonium as  $\text{PuF}_6$  and the reaction is used in removing plutonium as  $\text{PuF}_6$  from spent nuclear fuel. Chlorine, bromine and iodine form oxide in which the oxidation states of these halogens range from +1 to +7.

A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens,  $\text{I} > \text{Cl} > \text{Br}$ . The higher oxides of halogens tend to be more stable than the lower ones.

Chlorine oxides,  $\text{Cl}_2\text{O}$ ,  $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}_6$  and  $\text{Cl}_2\text{O}_7$  are highly reactive oxidising agents and tend to explode.  $\text{ClO}_2$  is used as a bleaching agent for paper pulp and textiles and in water treatment. The bromine oxides,  $\text{Br}_2\text{O}$ ,  $\text{BrO}_2$ ,  $\text{BrO}_3$  are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidising agents. The iodine oxides,  $\text{I}_2\text{O}_4$ ,  $\text{I}_2\text{O}_5$ ,  $\text{I}_2\text{O}_7$  are insoluble solids and decompose on heating.  $\text{I}_2\text{O}_5$  is a very good oxidising agent and is used in the estimation of carbon monoxide.

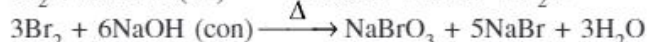
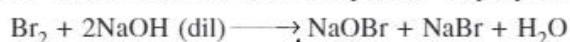


Reaction of  $\text{Cl}_2$ ,  $\text{Br}_2$  or  $\text{I}_2$  with water involves disproportionation

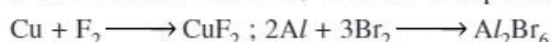
**With alkali :** Fluorine reacts with dilute alkali to give oxygen difluoride, but with hot concentrated alkali oxygen is liberated.



Chlorine, bromine and iodine react separately with dilute alkali to give hypohalite and halide. With hot concentrated alkali these halogens give halate and halide. These reactions are examples of disproportionation.



**With metals :** Metals react with halogens forming metal halides. Fluoride shows highest reactivity with metals. It even reacts with noble metals like gold, platinum, etc. Metal fluorides are ionic, with few exceptions like beryllium fluoride.



The ionic character of the halides decreases in the order :  $\text{MF} < \text{MCl} < \text{MBr} > \text{MI}$ . If a metal exhibits more than one oxidation state, the halide in higher oxidation state will be more covalent (eg :  $\text{SnCl}_4$  is more covalent than  $\text{SnCl}_2$ )

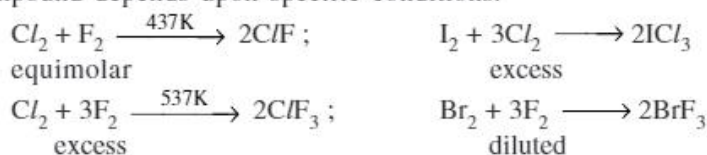
**With halogens :** Halogens react with each other forming binary compounds, called interhalogen compounds. Interhalogens are four types as listed in Table 3.6. Interhalogens are diamagnetic. Atomicity of an interhalogen compound is an even number and the highest atomicity is eight.

Binary compounds formed between halogens are called interhalogens

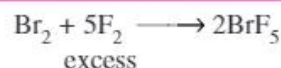
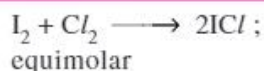
Table 3.6 Some Properties of Interhalogen Compounds

Type	Formula	Physical state and colour	Structure
$\text{XX}'_1$	$\text{ClF}$	colourless gas	Linear
	$\text{BrF}$	pale brown gas	Linear
	$\text{IF}^a$	detected spectroscopically	Linear
	$\text{BrCl}^b$	gas	Linear
	$\text{ICI}$	ruby red solid ( $\alpha$ -form)	Linear
	$\text{IBr}$	black solid	Linear
$\text{XX}'_3$	$\text{ClF}_3$	colourless gas	Bent T-shaped
	$\text{BrF}_3$	yellow green liquid	Bent T-shaped
	$\text{IF}_3$	yellow powder	Bent T-shaped
	$\text{ICI}_3$	orange solid	Bent T-shaped
$\text{XX}'_5$	$\text{IF}_5$	colourless gas	Square pyramidal
	$\text{BrF}_5$	colourless liquid	Square pyramidal
	$\text{ClF}_5$	colourless liquid	Square pyramidal
$\text{XX}'_7$	$\text{IF}_7$	colourless gas	Pentagonal bipyramidal

Interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product interhalogen compound depends upon specific conditions.







$\text{ClF}$  is colourless gas,  $\text{BrF}$  is pale brown gas while  $\text{ICl}$  is a red solid.  $\text{ClF}_3$  is colourless gas and is the common form in which fluorine is preserved.  $\text{IF}_3$  is yellow powder but  $\text{ICl}_3$  is orange solid. In solid state  $\text{ICl}_3$  exist as planar dimer  $\text{I}_2\text{Cl}_6$ .  $\text{IF}_5$  and  $\text{IF}_7$  are colourless gases, while  $\text{BrF}_5$  and  $\text{ClF}_5$  are colourless liquids.

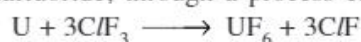
*Interhalogens  
are polar and  
more reactive*

Physical properties of interhalogen compounds are intermediate between those of constituent halogens, except the melting and boiling points are a little higher than expected. Interhalogen compounds have heteroatomic bonds. These bonds are polar and hence interhalogens are more reactive than halogens. However, the reactivity of interhalogen is less than that of fluorine.

Hydrolysis of interhalogens give halide ion derived from the smaller halogen and oxyanion derived from larger halogen.



Interhalogens are used as non aqueous solvents.  $\text{ClF}_3$  and  $\text{BrF}_3$  are used as fluorinating agents and in the enrichment of  $^{235}\text{U}$  by converting it to volatile uranium hexafluoride, through a process called atmolysis.



### 3.1.5

#### Oxidation ability

Electron affinity of halogen is high, hence, they are good oxidants. Fluorine is the best oxidising agent. The oxidation ability of halogens decreases from fluorine to iodine. Halogen atoms gain electrons and form halide ions. When halogens of lower molecular size react with halides of higher ionic size, the corresponding halides are formed.

Fluorine can displace all halides from their salts.



Chlorine cannot oxidise fluoride. It displaces bromide and iodide. Bromine can displace only iodide. Iodine cannot displace halides.



Fluorine, chlorine and bromine oxidise aqueous ferrous iron to ferric ion.



(Here  $\text{X}_2 = \text{F}_2, \text{Cl}_2$  or  $\text{Br}_2$ , but not  $\text{I}_2$ )

Iodine, however, is such a weak oxidising agent that it cannot remove electrons from ferrous ion.

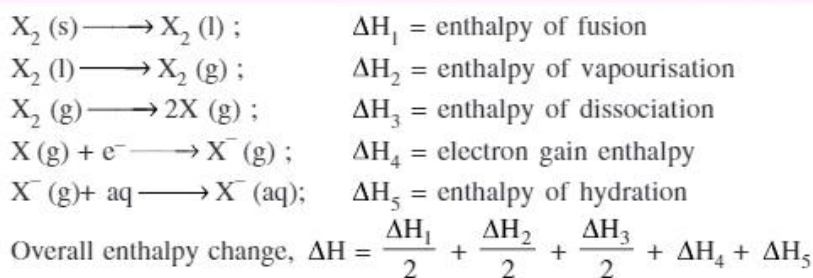
The standard reduction potentials of halogens are positive and decrease from fluorine to iodine. Thus the halogen that has highest reduction potential acts as strongest oxidant. With a decrease in the reduction potential, their oxidising ability decreases. Oxidation ability can also be explained with the net enthalpy change of the reaction. The enthalpy change in the reaction for the conversion of halogen to hydrated halide can be estimated by the application of Hess law using Born - Haber cycle.

*Iodine cannot  
oxidise  
ferrous iron*

*Fluorine has  
highest reduction  
potential and  
acts as hence  
oxidant*



*Oxidation ability  
decreases from  
fluorine to iodine*



Since enthalpy change is more negative for fluorine, it is the best oxidant. This is because of low bond dissociation energy of fluorine and high hydration energy of fluoride. From the results of Table 3.7, it is evident that the oxidation ability is in the order :  $F_2 > Cl_2 > Br_2 > I_2$ .

**Table 3.7 Energy cycle for different halogens (all energies in  $\text{kJ mol}^{-1}$ )**

Enthalpy change	Fluorine	Chlorine	Bromine	Iodine
Enthalpy of fusion	–	–	–	+1552
Enthalpy of vapourisation	–	–	+30	+42
Enthalpy of dissociation	+159	+243	+193	+151
Electron gain enthalpy	–333	–349	–325	–296
Enthalpy of hydration	–573	–370	–338	–272
Overall energy change	–767	–598	–537	–437

### 3.1.6

#### Anamolous behaviour of fluorine

Halogens are very reactive and act as good oxidants. Fluorine is the most reactive halogen and is called superhalogen. The following are the important points in which fluorine differs from the rest of the group VIIA elements.

1. Fluorine does not exhibit positive oxidation number in its compounds. It shows only –1 oxidation state, while other halogens exhibit positive oxidation states, ranging from +1 to +7.
2. Fluorine is always univalent in its compounds, while the other halogens are even heptavalent.
3. Fluorine is very reactive as the dissociation energy of F–F bond is low. But the Cl–Cl and Br–Br bonds are stronger.
4. Hydrogen fluoride is a liquid at  $20^\circ\text{C}$ , while the other hydrogen halides are gases at room temperature. Hydrofluoric acid is a weak acid, but aqueous HCl, HBr and HI are strong acids.
5. Silver fluoride is water soluble, but other silver halides are insoluble in water. Calcium fluoride is insoluble in water, while other calcium halides are water soluble.
6. Fluorine can displace all halides from their salts, while other halogens cannot displace all halides.
7. The only halogen that oxidises water to oxygen is fluorine. Its reaction with water is spontaneous. Other halogens form hydrohalic acid and hypohalous acid with water.

*Fluorine only  
displaces all  
halides from  
their salts*





Fluorine has  
no oxyacid

8. Fluorine can directly combine with carbon to form fluorocarbons, while other halogens cannot combine with carbon even in drastic conditions.
9. Fluorine can react even with inert gases like xenon. Other halogens do not react.
10. Though fluorine is the best non-metal, it has no oxyacid. Many oxyacids and oxysalts of chlorine, bromine and iodine are known.

The anomalous behaviour of fluorine and the difference in the properties listed above are mainly due to : (a) Small size of fluorine atom, (b) Absence of d-orbitals in the valence shell of fluorine, (c) Highest electronegativity of fluorine, (d) Low bond dissociation enthalpy of fluorine and Fluorine has only two electrons in its penultimate shell.



**P.3.1** Write on the electropositivity of iodine.

**Solution** All halogens are non-metals. Iodine is also a non-metal. However, iodine shows certain electropositivity.

The +1 state is more stable for iodine, as evidenced in molten  $\text{ICl}$  and molten  $\text{ICN}$

Only iodine is naturally available in positive oxidation states.  $\text{NaIO}_3$  is its mineral.

Iodine is the only halogen uses three d-orbitals for hybridisation,  $\text{sp}^3\text{d}^3$  in  $\text{IF}_7$ .



**P.3.2** Write the order of bond enthalpies of halogens. Why is it not opposite to that of bond lengths?

**Solution** Bond lengths of halogens are in the order :  $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$ .

But the experimental bond enthalpies are :  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$ .

Bond enthalpy of  $\text{F}_2$  is very less, because lone pair - lone pair repulsions are appreciable in  $\text{F}_2$  as the bond length is small in  $\text{F}_2$ .

It was also thought, though not appropriate, that F-F bond is weak as multiple bond is not possible with no d-orbitals in the valence shell of fluorine.



**P.3.3** Chlorine can exhibit -1 and +1 states, while fluorine can exhibit only -1, but not +1. Why?

**Solution** General valency of halogens is one. When chlorine (or bromine or iodine) is mono-valent, with more electronegative elements, it exhibits +1 state.

Fluorine can never exhibit positive oxidation state as it is the most electronegative element.



**P.3.4** Iodine is violet coloured. Why?

**Solution** Iodine is a bigger molecule, in which the valence electrons are not held very strong by the nuclei in the molecule. It absorbs low energy orange - red radiation of visible light and reflects its complimentary colour. Hence iodine is violet coloured.



**P.3.5** Standard reduction potential (SRP) of fluorine is highest. Comment.

**Solution** Standard potential for the reaction,  $\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$  is highest, +2.87 V.

This is because, fluoride is the easiest formed anion from its element and hydration enthalpy is highest for fluoride. Highest SRP suggests that fluorine is the best oxidant.



**P.3.6** Among the reactions,  $\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{g})$  and  $\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{g})$ , which is more feasible? Give the reason.

**Solution** The reaction,  $\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{g})$ , is more feasible.

Formation of halide from halogen involves bond dissociation enthalpy and electron gain enthalpy. Electron gain enthalpy is more for chlorine and its bond dissociation energy is also more. Hence, it is relatively difficult to form chloride.





**P.3.7** Electron gain enthalpy of fluorine is less than that of chlorine. Why?

**Solution**

Fluorine atom is small in size and suffers with interelectronic repulsions between seven valence electrons. The added electron experiences much repulsion on smaller F. Hence its electron gain enthalpy is less.



**P.3.8** Heavier halide is oxidised by lighter halogen. Justify.

**Solution**

The oxidation ability of halogens is in the order :  $F_2 > Cl_2 > Br_2 > I_2$ .

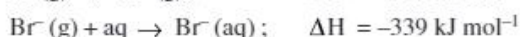
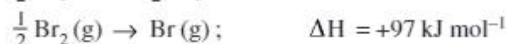
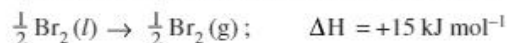
Lighter halogen is a stronger oxidant. Heavier halide is less stable, acts as a reducing agent and is easily oxidised.

The reaction that is easily possible among halides and halogens is,  $2I^- + F_2 \longrightarrow 2F^- + I_2$



**P.3.9** Bond enthalpy of bromine is  $194 \text{ kJ mol}^{-1}$ . If enthalpy of vapourisation of  $Br_2$  is  $+30 \text{ kJ mol}^{-1}$ , electron gain enthalpy of Br is  $-325 \text{ kJ mol}^{-1}$  and hydration enthalpy of bromide is  $-339 \text{ kJ mol}^{-1}$ , calculate the change in enthalpy for the reaction,  $\frac{1}{2} Br_2(l) + e^- \xrightarrow{aq} Br^-(aq)$ .

**Solution**



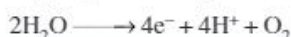
Adding these equations we get,  $\frac{1}{2} Br_2(l) + e^- \xrightarrow{aq} Br^-(aq); \Delta H = -552 \text{ kJ mol}^{-1}$



**P.3.10** Electrolysis of aqueous HF produces  $O_2$  at anode but not  $F_2$ . Explain.

**Solution**

In aqueous solution, fluoride ( $F^-$ ) is very stable. Electrolysis of aqueous fluoride liberates oxygen, due to the preferential oxidation of water.



### EXERCISE - 3.1.1

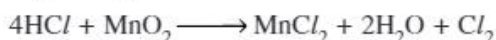
1. Discuss the electronic configuration of halogens.
2. Write on the occurrence and important minerals of halogens.
3. Discuss the following trends in halogens :  
(a) atomic radius, (b) electron affinity and (c) electronegativity.
4. Compare the reactivity halogens with hydrogen. Discuss
5. How does halogens react with (a) water (b) alkali and (c) metals?
6. Write a note on bonding and structures of interhalogen compounds.
7. Discuss on the oxidation ability of halogens.
8. Write the distinction between fluorine and rest of the halogens.

## CHEMISTRY OF CHLORINE

### 3.2.1

#### Isolation

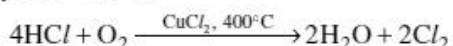
Chlorine is naturally available as chloride. Scheele was first to prepare chlorine, by the oxidation of chlorides. Chlorine is prepared in the laboratory by the oxidation of hydrochloric acid. The oxidising agents used are manganese dioxide, potassium permanganate, potassium dichromate and bleaching powder.





*Chlorine is prepared on a large scale by the electrolysis of brine solution*

Bulk isolation of chlorine in commercial scale also involves the oxidation of chloride. In Weldon's process, pyrolusite mineral ( $\text{MnO}_2$ ) is heated with concentrated hydrochloric acid, to obtain chlorine. In Deacon's process, chlorine is prepared by the atmospheric oxidation of hydrochloric acid in the presence of cupric chloride catalyst at  $400^\circ\text{C}$ .



Electrolysis of brine solution in Nelson's cell or Castner-Kellner's cell is a modern method of preparing chlorine on a large scale. Down's process is also used for the commercial production of chlorine.

### 3.2.2

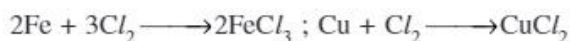
#### Properties

Chlorine is pungent odoured gas with greenish yellow colour. It is about 2.5 times heavier than air. Chlorine has pungent odour. It is pollutant, poisonous and effects mucous membrane. On freezing chlorine gives yellow liquid and finally pale yellow solid. Chlorine is also a very reactive element.

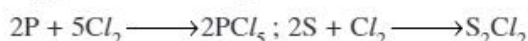
**1. Reaction with hydrogen :** Chlorine reacts with hydrogen in diffused light to form hydrogen chloride. With compounds containing hydrogen it gives hydrogen.



**2. Reaction with metals :** Chlorine reacts with all metals, except noble metals. It forms metal chlorides. Iron can form two halides with chlorine, but the metal on reaction directly with chlorine forms a compound with its highest stable oxidation state. Hence union of iron with chlorine gives ferric chloride. Similarly with copper, cupric chloride is formed.



**3. Reaction with non-metals :** Chlorine reacts with non-metals except nitrogen and oxygen at room temperature to form non-metal chlorides.



**4. Reaction with water :** Chlorine reacts with water forming hydrochloric and hypochlorous acids.



Hypochlorous acid is unstable and decomposes to give nascent oxygen. Thus moist chlorine acts as oxidant and bleaching agent.

**5. Reaction with halides :** Chlorine does not oxidise fluoride, but liberates bromine and iodine from their respective aqueous halide salts.



**6. Reaction with alkali :** Chlorine reacts with dilute alkali at room temperature forming chloride and hypochlorite. With hot, concentrated alkali chlorine forms chloride and chlorate.



*Metal reacts with chlorine to form compound with highest stable oxidation state*

*Moist chlorine acts as oxidant and bleaching agent*



*Addition product of chlorine and carbon monoxide is a war gas*

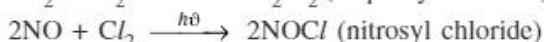
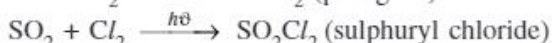
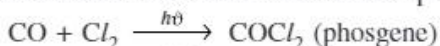
*Chlorine oxidises sulphite and thiosulphate to sulphate*

*Chloropicrine called tear gas*

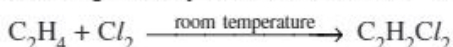
**7. Reaction with ammonia :** Chlorine reacts with excess ammonia to form nitrogen and ammonium chloride. Excess chlorine gives nitrogen trichloride and ammonium chloride.



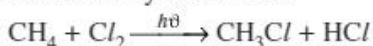
**8. Addition reactions :** Chlorine forms addition compounds with carbon monoxide sulphur dioxide and nitric oxide in the presence of sunlight.



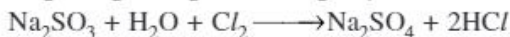
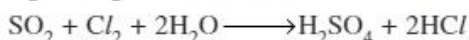
Chlorine also adds on to unsaturated hydrocarbons. Chlorine reacts with ethylene to give ethylenedichloride and with acetylene gives westron.



**9. Oxidation ability :** Chlorine is a good oxidising agent. It oxidises bromides to bromine, iodides to iodine, ferrous salts to ferric salts. It gives substitute products with saturated hydrocarbons.



Moist chlorine oxidises vegetable colouring matter and bleaches it. Chlorine oxidises hydrogen sulphide to sulphur and sulphur dioxide to sulphuric acid. It oxidises sulphite to sulphate and aqueous iodine to iodate.



### 3.2.3

#### Uses

Chlorine is a good oxidising agent. It is used in the sterilisation of water, because it kills bacteria.

It is used in manufacturing bleaching powder and as a bleaching agent for wood pulp, cotton, rayon or linen.

It is used in the extraction of noble metals like gold and platinum.

It is used in the preparation of solvents like carbon tetrachloride, chloroform, ethylene dichloride and acetylene tetrachloride; refrigerants like freons; insecticides like DDT (dichlorodiphenyl trichloroethane) and BHC (benzene hexachloride); plastics like PVC (polyvinyl chloride) and neoprene rubber.

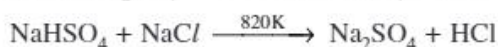
It is used in the preparation of poisonous gases of the war-fare like, phosgene, also called carbonyl chloride ( $\text{COCl}_2$ ), tear gas, also called nitrochloroform or chloropicrine ( $\text{CCl}_3\text{NO}_2$ ), mustard gas ( $\text{ClC}_2\text{H}_4\text{S-C}_2\text{H}_4\text{Cl}$ ), lewisite ( $\text{ClCH} = \text{CHAsCl}_2$ ), etc.

### 3.2.4

#### Hydrogen chloride

Hydrogen chloride was first prepared by Glauber, by heating common salt with con-centrated sulphuric acid. The same method is used in laboratory to prepare it now-a-days.

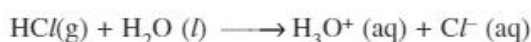




Hydrogen chloride gas can be dried by passing the gas through concentrated sulphuric acid.

*HCl gas is dried over conc.  $\text{H}_2\text{SO}_4$*

Hydrogen chloride is a colourless and pungent odoured gas. It is easily liquefied to a colourless liquid and freezes to a white crystalline solid at 159 K. It is extremely soluble in water and forms acid. Hydrochloric acid is a strong acid and the  $\text{pK}_a$  for its ionisation in water is  $-7$ .

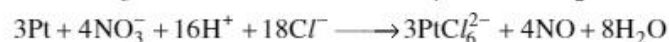


Hydrochloric acid reacts with ammonia and gives white fumes.

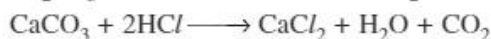
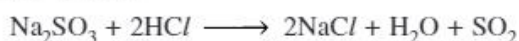


*Aqua-regia is a 3:1 mixture of conc. HCl and conc.  $\text{HNO}_3$*

Aqua-regia is a mixture of three parts of concentrated hydrochloric acid and one part of concentrated nitric acid. This mixture is used to dissolve noble metals like gold and platinum.



Hydrochloric acid decomposes salts of weaker oxyacids to liberate acidic gaseous oxides.



Hydrogen chloride is used in the manufacture of chlorine, ammonium chloride and glucose from corn starch. Hydrochloric acid is also used as a laboratory reagent, in medicine, in extracting glue from bones and purifying bone black.

### 3.2.5

#### Bleaching Powder

*Oxidation numbers of chlorine in bleaching powder are  $-1$  and  $+1$*

Bleaching powder is known as chlorine of lime. It is assumed as a mixed salt of hydrochloric acid and hypochlorous acid. Bleaching powder may be called calcium chlorohypochlorite. Bleaching powder is prepared on a large scale by the action of chlorine on dry slaked lime.



Composition of bleaching powder is also given as  $\text{Ca(OCl)}_2 \cdot \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O}$ . The oxidation numbers of chlorine in bleaching powder are  $-1$  and  $+1$ .

Bleaching powder is commonly used as a bleaching agent for cotton and pulp. It is used as germicide, a disinfectant and a sterilising agent. It is used to purify water. Bleaching powder is used in the preparation of chloroform from ethyl alcohol, acetaldehyde or from acetone. It is used as an oxidising agent and a chlorinating agent.



#### P.3.11

What is the action of litmus with aqueous chlorine?

#### Solution

Aqueous chlorine turns blue litmus to red and finally colourless. It also turns red litmus colourless.

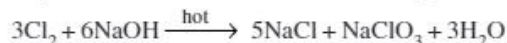
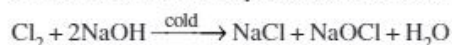
This is because of the fact that aqueous chlorine is acidic and also acts as a bleaching agent.





**P.3.12** What kind of reaction that chlorine undergoes with aqueous alkali solution ?

**Solution** Chlorine reacts with aqueous caustic soda in different conditions.



Chlorine undergoes disproportionation with alkali. Chlorine is reduced to chloride and simultaneously oxidised to hypochlorite or chlorate.



**P.3.13**  $\text{Cl}_2$  is more reactive than  $\text{I}_2$  but when  $\text{KClO}_3$  reacts with  $\text{I}_2$ ,  $\text{Cl}_2$  is liberated. Why ?

**Solution** Reaction of chlorate with iodine is a redox reaction and  $\text{I}_2$  is oxidised.



**P.3.14** When  $\text{HCl}$  reacts with powdered iron, ferrous chloride is formed, but not ferric chloride. Why?

**Solution** Reaction of iron with hydrochloric acid produces ferrous chloride and liberate hydrogen.



This liberated hydrogen prevents the formation of ferric chloride.



**P.3.15** What happens when some ethyl alcohol is added in the Nelson's cell and the cell is closed?

**Solution** The main products in the Nelson's cell are chlorine and caustic soda.

Ethyl alcohol is first oxidised with chlorine to acetaldehyde and then to chloral.

Chloral on base hydrolysis gives chloroform.

### EXERCISE - 3.1.2

1. Describe the Nelson's cell method for the preparation of chlorine.
2. Write the general chemical properties of chlorine.
3. How does chlorine react with hydrocarbons? Write the necessary chemical equations.
4. Mention the important uses of chlorine.
5. How is hydrogen chloride prepared? Write its uses.
6. What is the composition of bleaching powder? How is it prepared.

## OXIDES AND OXYACIDS OF CHLORINE

### 3.3.1

#### Oxides

The binary compounds of oxygen and in which oxidation states of halogens range from fluorine are called fluorides ( $\text{OF}_2$  and  $\text{O}_2\text{F}_2$ ). Only  $\text{OF}_2$  is thermally stable at 298 K.

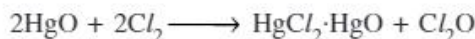
Chlorine oxides,  $\text{Cl}_2\text{O}$ ,  $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}_6$  and  $\text{Cl}_2\text{O}_7$  are highly reactive oxidising agents and tend to explode. Oxides of chlorine are important and are listed in Table 3.8.

Table 3.8 Oxides of chlorine

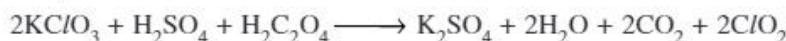
Name of the oxide	Chemical formula	Oxidation state of chlorine	Colour	Physical state
Chlorine monoxide	$\text{Cl}_2\text{O}$	+1	Yellow	Gas
Chlorine dioxide	$\text{ClO}_2$	+4	Dark Yellow	Gas
Chlorine hexoxide	$\text{Cl}_2\text{O}_6$	+6	Red	Liquid
Chlorine heptoxide	$\text{Cl}_2\text{O}_7$	+7	Colourless	Liquid



**Preparation :** Chlorine monoxide is prepared by the action of chlorine on freshly prepared mercuric oxide.



Chlorine dioxide is prepared by the action of a mixture of sulphuric acid and oxalic acid on potassium chlorate. Oxalic acid in this reaction not only acts as a reductant, but also as a diluant.



Chlorine hexoxide is prepared by the action of ozone on chlorine dioxide.

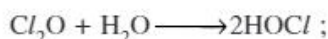


Chlorine heptoxide is prepared by the dehydration of perchloric acid with phosphoric acid at  $-10^\circ\text{C}$ , followed by distillation under reduced pressure.



**Nature :** All these oxides are covalent and acidic. Acidic nature increases with an increase in the oxidation number of chlorine. Chlorine heptoxide is the most acidic oxide. Chlorine monoxide is a bleaching agent. In solid state  $\text{Cl}_2\text{O}_6$  exist as a mixture of  $\text{ClO}_2^+$  and  $\text{ClO}_4^-$ .

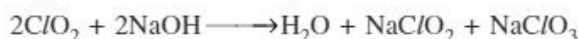
Oxides of chlorine undergo hydrolysis to give oxyacids.



Chlorine monoxide is the anhydride of hypochlorous acid and chlorine heptoxide is the anhydride of perchloric acid. Chlorine dioxide is a mixed anhydride of  $\text{HClO}_2$  and  $\text{HClO}_3$ . Chlorine hexoxide is also a mixed anhydride of  $\text{HClO}_3$  and  $\text{HClO}_4$ .

The acidic nature of these oxides is supported by the formation of corresponding salts with alkali.

Chlorine monoxide dissolves in alkali to form hypochlorite, chlorine dioxide forms chlorite and chlorate, chlorine hexoxide forms chlorate and perchlorate and chlorine heptoxide forms perchlorate.



**Reactivity :** Chlorine dioxide is very reactive chemically because of the presence of unpaired electron. It is paramagnetic. Chlorine trioxide ( $\text{ClO}_3$ ) also has unpaired electron and paramagnetic, but the dimeric form, chlorine hexoxide ( $\text{Cl}_2\text{O}_6$ ) is diamagnetic due to the presence of paired electrons. Chlorine hexoxide is explosive and unstable. It decomposes to give chlorine dioxide and oxygen. All the oxides of chlorine act as good oxidants. Oxidation ability is highest for chlorine monoxide.

Chlorine heptoxide is the most acidic oxide

Oxides of chlorine give oxy acids upon hydrolysis

Chlorine dioxide is paramagnetic



*Cl<sub>2</sub>O is angular  
with angle 111°  
ClO<sub>2</sub> is angular  
with angle 117°*

**Structures :** Chlorine monoxide is angular. The central atom oxygen undergoes sp<sup>3</sup> hybridisation. The Cl/OCl bond angle is 111°. This angle is greater than the tetrahedral angle due to the steric repulsions between large chlorine atoms.

Chlorine dioxide is also angular. The molecule contains odd number of electrons. The Cl–O bond length lies in between a single bond length and a double bond length. The OClO bond angle is 117°. The structure is considered to be a resonance hybrid.

Chlorine heptoxide is assigned a bitetrahedral structure based on the electron diffraction and infrared spectral studies. The two ClO<sub>4</sub> tetrahedral units are joined through one 'O' atom. The Cl/OCl bond angle is 115° and OClO bond angle is 97°.

## 3.3.2

## Oxyacids

Due to high electronegativity and small size, fluorine forms only one acid, HOF known as hypofluorous acid or fluoric (I) acid. Chlorine has four oxyacids. The oxyacids of halogens are listed in Table 3.9. Bromine and iodine each forms three types of oxyacids : hypohalous acid, halic acid and perhalic acid.

Table 3.9 Oxyacids of halogens

Halogen	Halic (I) acid (Hypohalous acid)	Halic (III) ACID (Halous acid)	Halic (V) acid (Halic acid)	Halic (VII) ACID (Perhalic acid)
Fluorine	HOF (Hypofluorous acid)	–	–	–
Chlorine	HOCl (Hypochlorous acid)	HOClO (Chlorous acid)	HOClO <sub>2</sub> (Chloric acid)	HOClO <sub>3</sub> (Perchloric acid)
Bromine	HOBr (Hypobromous acid)	HOBrO (Bromous acid)	HOBrO <sub>2</sub> (Bromic acid)	HOBrO <sub>3</sub> (perbromic acid)
Iodine	HOI (Hypoiodous acid)	–	HOIO <sub>2</sub> (Iodic acid)	HOIO <sub>3</sub> (Periodic acid)

The oxyacids of chlorine are more acidic than those of bromine and iodine. With a decrease in the electronegativity of halogen, the acidic strength of the oxyacid decreases.

**Preparation :** Hypochlorous acid is prepared by mixing chlorine water with freshly prepared mercuric oxide.



Chlorous, chloric and perchloric acids are prepared by the action of a dilute mineral acid on the corresponding salts.

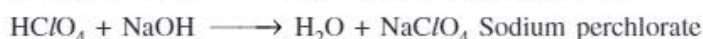
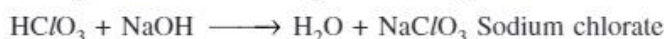
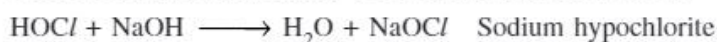


**Nature :** All these acids are monoprotic. The acidic nature increases with an increase in the oxidation number of halogen. Perchloric acid exhibits highest acidic nature among all acids. Acidic strength is more for the acid formed by chlorine HOCl > HOBr > HOI.

*Acidic nature of  
oxyacids  
increases with  
increase in  
oxidation state*



These acids neutralise alkali to form corresponding salts.



**Oxidising ability :** Hypochlorous acid is unstable. It decomposes readily to provide nascent oxygen.

Due to the availability of nascent oxygen, hypochlorous acid acts as a very good oxidising agent. It is also a good bleaching agent based on its oxidation ability.

Thermal stability of the anions of these acids gradually increases from hypochlorous acid to perchloric acid. Therefore, oxidising ability and bleaching ability decrease gradually. Perchloric acid almost does not act as oxidising agent. It is not a bleaching agent.

**Structures :** Chlorine undergoes  $sp^3$  hybridisation in all these oxyacids. The anion of the oxyacid and the corresponding structure are listed in Table 3.10 and the structures are shown in Fig 3.2.

Table 3.10 Oxyanions of chlorine

Anion	Formula	Structure	Cl-O bond length	Cl-O bond energy	Bond angle
Hypochlorite	$\text{OCl}^-$	Linear	170 pm	$209 \text{ kJ mol}^{-1}$	—
Chlorite	$\text{ClO}_2^-$	Angular	164 pm	$245 \text{ kJ mol}^{-1}$	$111^\circ$
Chlorate	$\text{ClO}_3^-$	Pyramidal	157 pm	$294 \text{ kJ mol}^{-1}$	$106^\circ$
Perchlorate	$\text{ClO}_4^-$	Tetrahedral	145 pm	$364 \text{ kJ mol}^{-1}$	$109.5^\circ$

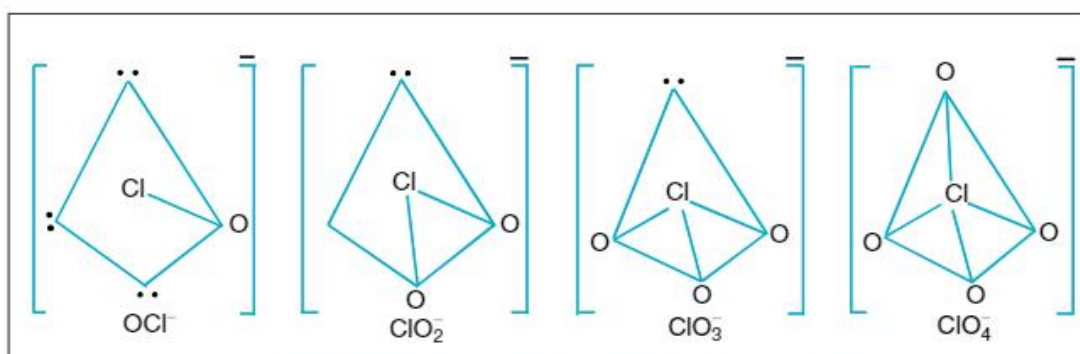
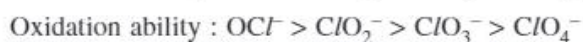
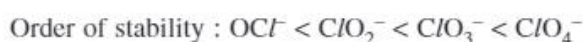


Fig 3.2 Structure of anions of chlorine oxyacids

Except in hypochlorite, all these anions are stabilised by resonance structures. Perchlorate ion has four canonical structures and is most stable. Perchloric acid ionises readily and acts as strongest acid.



*Hypochlorous acid is good oxidant and bleaching agent*

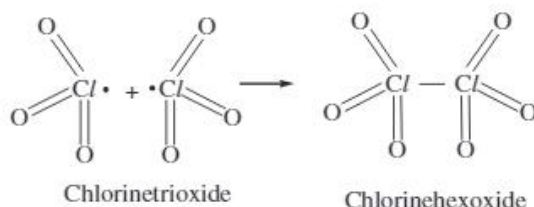
*HClO<sub>4</sub> is the strongest acid*





**P.3.16** Chlorine trioxide is paramagnetic, but chlorine hexoxide is diamagnetic. Explain.

**Solution** Chlorine trioxide,  $\text{ClO}_3$  has unpaired electron. Hence it is paramagnetic. Upon dimerisation, chlorine hexoxide is formed.  $\text{Cl}_2\text{O}_6$  has all paired electrons. It is diamagnetic.



**P.3.17** Hypochlorite is a strong oxidant and bleaching agent. Why ?

**Solution** Hypochlorite,  $\text{OCl}^-$  is formed in the ground state of oxygen.  $\text{O}-\text{Cl}$  bond is a single bond.  $\text{OCl}^-$  has no tendency to form pi bond and also it is not stabilised by resonance. It is less stable and provides nascent oxygen by decomposition.



Hence,  $\text{OCl}^-$  hypochlorite is good oxidant and powerful bleaching agent.



**P.3.18** Perchloric acid is strongest acid, but weakest oxidising agent. Why?

**Solution**  $\text{HClO}_4$  has  $\text{pK}_a < -10$ . Its ability to provide proton is highest. This is due to resonance stabilisation of perchlorate ion.  $\text{ClO}_4^-$  has four canonical structures and six delocalised pi electrons.

$\text{ClO}_4^-$  is resonance stabilised. It does not furnish oxygen and hence a weak oxidant.



**P.3.19** Iodine is liberated in the reactions between KI and  $\text{Cu}^{2+}$ , but chlorine is not liberated when KCl is added to  $\text{Cu}^{2+}$ , why?

**Solution** Iodide is a strong reducing agent. Though  $\text{Cu}^{2+}$  is a mild oxidising agent, iodide reduces  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  ion. Chloride is a weak reducing agent. It does not reduce  $\text{Cu}^{2+}$  ion.



**P.3.20** What are pseudohalides, polyhalides and pseudohalogens?

**Solution** Pseudohalides are univalent negatively charged ions, which behave like halides. eg : Cyanide,  $\text{CN}^-$ ; thiocyanide,  $\text{SCN}^-$ , etc.

Polyhalides are monovalent anions, formed by 3 or more halogen atoms. eg :  $\text{I}_3^-$ ,  $\text{ICl}_4^-$ , etc.

Pseudohalogens are dimeric neutral units of pseudohalides. eg : Cyanogen,  $\text{C}_2\text{N}_2$

### EXERCISE - 3.1.3

1. Mention different oxides of chlorine. Discuss their acidic nature.
2. Write various oxyacids formed by halogens.
3. Write the oxidation numbers of chlorine in its oxyacids.
4. Discuss the structures of oxyanions of chlorine. Compare the  $\text{O}-\text{Cl}$  bond lengths and bond energies.





1. Fluorine, chlorine, bromine and iodine are the elements of group 17 and are called halogens.
2. The general electronic configurations of group VII A elements is  $ns^2np^5$ .
3. Fluorine and chlorine are gases at room temperature. Bromine is a liquid and iodine is a solid.
4. Sea is a potential source of halogens. Chlorine is the most abundant halogen in earth's crust. Halogens are generally available as halides.
5. Halogens are all diatomic molecules. Astatine is monoatomic, synthetic and radioactive.
6. All halogens are non-metals. Electropositivity increases down the group.
7. Bond lengths increase from  $F_2$  to  $I_2$ , but bond energies are in the order :  $Cl_2 > Br_2 > F_2 > I_2$ .
8. Fluorine does not exhibit positive oxidation states. The universal oxidation state of fluorine in its compounds is  $-1$ .
9. Fluorine is monovalent. Other halogens can even exhibit heptavalency in the highest excited state.
10. Among all elements, electronegativity is highest for fluorine and electron affinity is highest for chlorine.
11. Standard reduction potential is highest for fluorine. It is the best oxidant. Oxidation ability decreases from fluorine to iodine.
12. Fluorine is the most reactive element. This is because of low bond dissociation energy of fluorine and high hydration enthalpy of fluoride.
13. Fluorine oxidises water to oxygen and ozone and forms hydrogen fluoride.
14. Fluorine displaces all halides from their salts. Chlorine cannot displace fluoride. Bromine can displace only one halide, iodide.
15. Compounds formed between two different halogens are called interhalogen compounds.
16. Chlorine is prepared on a large scale by the electrolysis of brine solution in Nelson's cell method.
17. Chlorine oxidises bromide to bromine and iodide to iodine.
18. Chlorine reacts with dry slacked lime giving bleaching powder.
19. Bleaching powder is regarded as a mixed salt of hydrochloric acid and hypochlorous acid. The oxidation number of chlorine in  $CaOCl_2$  are  $+1$  and  $-1$ .
20. Aqua-regia is a 3: 1 mixture of concentrated and concentrated nitric acid. This mixture dissolves metals like gold and platinum.



21. Chlorine heptoxide is the most acidic oxide.
22. The strongest acid is perchloric acid,  $\text{HClO}_4$ .
23. Hypochlorous acid or hypochlorite acts as good oxidant and bleaching agent, as it provides nascent oxygen.
24. From hypochlorite to perchlorate ion, chlorine-oxygen bond energy increases and stability of anion also increase.

**EXERCISE - 3.2**

1. Why elements of group 17 are called halogens?
2. Write on the atomicity and bonding of halogen molecules.
3. Fluorine is always monovalent, but other halogens can exhibit valencies 1, 3, 5 and 7. Explain.
4. Which element brings about highest coordination number of elements? Why?  
(Ans : Fluorine)
5. Iodine exhibits basic properties. Explain.
6. Differentiate the products of water on reaction with fluorine and chlorine.
7. Discuss the oxidation states of chlorine in its compounds.
8. Explain the trends in ionisation potential, electron affinity, electronegativity and metallic nature of halogens.
9. Discuss the ease of formation of hydrogen halides. Write the trends in their thermal stability and volatility.
10. How do halogens react with water? Give chemical equations.
11. Discuss the difference in the reactions of halogens with cold dilute alkali and hot concentrated alkali.
12. Discuss the feasibility of oxidising halides, using halogens, sulphuric acid and manganese dioxide.
13. What are interhalogen compounds? Discuss on the types of these compounds.
14. Explain with suitable examples that the oxidation ability of halogens decreases from fluorine to iodine.
15. With the help of Born-Haber cycle, explain the chemical reactivity of halogens.
16. The oxidation of fluoride is very difficult to perform. Why?
17. Iodine is liberated in the reaction between  $\text{KI}$  and  $\text{Cu}^{2+}$ , but bromine is not liberated when  $\text{KBr}$  is added to  $\text{Cu}^{2+}$ . Explain.
18. Interhalogen compounds are more reactive than the corresponding halogens. Explain.
19. Phosphoric acid is preferred in place of sulphuric acid in the preparation of hydrogen iodide from alkalimetal iodide. Why?



20. Fluorine is called super halogen. Why?
21. How is chlorine prepared in the laboratory and on a commercial scale?
22. How does chlorine react with (a) Fe, (b)  $\text{H}_2\text{O}$  and (c)  $\text{H}_2\text{S}$ ? Give equations?
23. Write the addition reactions of chlorine with (a) non-metal oxides and (b) unsaturated hydrocarbons.
24. What makes gold to dissolve in aqua-regia?
25. How is chlorine used (a) in bleaching, (b) as disinfectant and (c) in war gases?
26. Ferric chloride  $\text{FeCl}_3$  is stable, but ferric iodide  $\text{FeI}_3$  is unstable. Explain.
27.  $\text{ClF}_3$  exists but not  $\text{FCl}_3$ . Substantiate.
28. HI is prepared from NaI, using  $\text{H}_3\text{PO}_4$  but not  $\text{H}_2\text{SO}_4$ . Explain.
29. Mention the action of blue litmus by hypochlorous acid.
30. Although oxygen contentent is high in perchlorate, it does not act as oxidant. Substantiate.
31. Red roses on exposure to moist chlorine permanently turns colourless. Explain.
32.  $\text{Na}_2\text{CO}_3 + \text{HCl} \longrightarrow \text{H}_2\text{O} + \text{NaCl} + \text{'X'}$  ;  
 $\text{'X'} + \text{Na}_2\text{S} \xrightarrow{\Delta} \text{S} + \text{'Y'}$  and  $\text{'Y'} + \text{I}_2 \longrightarrow \text{NaI} + \text{'Z'}$   
 In the above sequence, the compound Z is a salt of which oxyacid? (Ans :  $\text{H}_2\text{S}_4\text{O}_6$ )
33.  $\text{NH}_4\text{Cl} + \text{NaOH} \longrightarrow (\text{Gas A})$  ;  $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow (\text{Gas B})$   
 Discuss the acid-base nature of these gases, when dissolved in water. What is the product formed between these gases when mixed together? (Ans :  $\text{NH}_4\text{Cl}$ )
34. A metal halide X on treating with copper sulphate solution yields a brown precipitate Y. Y turns colourless on adding with hypo. What are X and Y? (Ans :  $\text{X} = \text{I}^-$ ,  $\text{Y} = \text{I}_2$ )
35. A liquid 'A' on treating with sodium carbonate solution gives a mixture of two salts 'B' and 'C'. The mixture on distillation with sulphuric acid produces 'A'. If 'A' is halogen, What are 'B' and 'C'? (Ans : NaBr and  $\text{NaBrO}_3$ )
36. Gradual addition potassium iodide with nitric acid produces a dark brown precipitate 'A'. 'A' is soluble in excess KI and gives yellow solution 'B'. What are A and B? (Ans :  $\text{A} = \text{I}_2$  ;  $\text{B} = \text{KI}_3$ )
37.  $\text{NaCl} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} + \text{X}$ .  
 Write the oxidation state of chromium in the product compound X. (Ans : +6)
38. A black power (X) when treated with common salt and chamber acid gives off a greenish-yellow gas (Y). Y on passing through boiling potash yields compounds are of which when heated with X evolves oxygen. What are X and Y? (Ans :  $\text{MnO}_2$ ,  $\text{Cl}_2$ )

