p–Block Elements

PHYSICAL PROPERTIES

1. PHYSICAL STATE AND MOLECULAR STRUCTURE

(i) Oxygen is the first member of group 16.

(ii) It is a gas while all other elements of the group are solids at ordinary temperature, as they form pπ – pπ overlapping.

(iii) The higher elements of the group S and Se etc. are unable to form pπ – pπ bonds due to their larger atomic size. Therefore these elements of the group link their atoms of by single bonds to form poly atomic complex molecules.

2. ATOMIC AND IONIC RADII

(i) The atomic radii of group 16 elements are smaller than those of the corresponding elements of group 15.

(ii) The atomic and ionic radii increase down the group. This is due to the addition of a new shell at each successive element on moving down the group.

3. DENSITY

(i) The density of group 16 elements increase on moving down the group.

4. ELECTRONEGATIVITY

(i) The elements of group 16 have highes values of electronegativity as compared to those of the corresponding elements of group 15.

(ii) Oxygen is the second most electronegative element.

(iii) Electronegativity decreases on moving down the group.

(iv) Electronegativity decrease from ‘O’ to Po.

5. MELTING POINT AND BOILING POINTS

(i) Melting point and boiling points increase regularly on moving down the group.

(ii) However the melting point and boiling point of polonuim are lower than that of lelluruim. Increase of melting and boiling point is due to increase of atomic size and increase is the magnitude of van der Weals forces.

(iii) The large difference between melting and boiling point of oxygen and sulphur is due to existence of oxyen as diatomic (O_2) molecule and sulphur as octatomic (S_8)

(iv) Pollonium possesses lower melting and boiling points than telluruim due to inert pair effect. Inert pair is maximum in polonium.

6. IONISATION ENTHALY OR IONIZATION ENERGY : (I.E.)

(i) Ionisation enthalpy of group 16 elements are quite high and it is very difficult to remove electrons from the valence shell of the atom. The ionization enthalpy decreases on moivng down the group.

(ii) Ionization enthalpy of group 16 is lower that of group 15.

7. ELECTRON GAIN ENTHALPY

(i) The electron gain enthalpy of oxygen is less negative than that of sulphur.

(ii) Electron gain enthalpy values decrease on moving down the group from sulphur to polonium.

8. METALLIC CHARACTER :

(i) Non-metallic character is stronger is Oxygen and sulphur and weaker is selenium and tellurium.

(ii) Metallic character increases down the group.

9. CATENATION :

(i) Oxygen shows only a littel tendency towards catenation.

(ii) The catenation tendency decreases on moving down the group from S to P0.

10. ALLOTROPY

(i) Oxygen exists as dioxygen (O_2) and ozone (O_3) the oxygen being most stable than ozone.

(ii) Sulphur exists is several alltropic modification α–sulphur, β–sulphur, γ–sulphur, homocycle sulphur, plastic sulphur, etc.

(iii) Selenium exists in many allotropic modifications like in crystalline form red monoclenic and grey metallic is amorphous form dark brown, vitrous and red amorphous selenuim etc.

(iv) Telluruim and polonium also show allotropy. Telluim exists in two allotropic modificaitons metallic and non-metallic. Poloniun has two forms namely α–form and β–form, both are metallic in nautre.

11. OXIDAITON STATE

(i) The characteristic electronic configuration of elements $ns^2\ np^4$ suggests the oxidations states –2, +2, +4 and +6.

(ii) The most common oxidation state of oxygen is –2 except in

$$\underset{(+2)}{OF_2} \quad \underset{(+1)}{O_2F_2} \quad \underset{(-1)}{H_2O_2}$$

(iii) Except oxygen, other elements have empty and d-orbitals, hence due to the unpairing transfer of electrons into d-orbitals, they exhibit +4 oxidation state. Eq : SF_4, $TeCl_4$, $SeBr_4$, etc.

CHEMICAL PROPERTIES

(a) All the lements of group 16 are reactive but reactivity decreases with increase in atomic number.

(i) Action of air : Elemente of group 16 are not affected by dry air at room temperature, but on heating they form dioxides

$$S + O_2 \longrightarrow SO_2 \quad Se + O_2 \longrightarrow SeO_2$$

(ii) Action of acids : They are unaffected by nonoxidizing acids sulphur is oxdized by hot conc^n. HNO_3 to sulphuric acid & selenium to selenous acid

$$S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

$$Se + 4HNO_3 \rightarrow H_2SeO_3 + 4NO_2 + H_2O$$

(iii) Action of alkalies : S, Se & Te dissolve in alkalies. Sulphur reacts with concentrated solution of alkali and forms sulphides and sulphites.

$$3S + 6NaOH \rightarrow Na_2SO_3 + 2Na_2S + 3H_2O$$

(iv) Action of Non-metals : Elements combine directly with C, H, X. (Carbon, Hydrogen, Halogen)

$$2S + C \longrightarrow CS_2$$

$$Se + 2Cl_2 \longrightarrow SeCl_4$$

$$S + H_2 \longrightarrow H_2S$$

(v) Action of metals : Form sulphides, selenides and tellurides when heated with S, Se & Te.

$$Cu + S \longrightarrow CuS$$

$$Cd + Se \longrightarrow CdSe$$

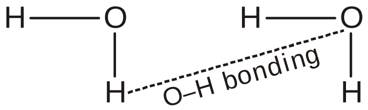
(b) Hydrides, Halides and Oxides :

(i) Reactivity with hydrogen and Physical states and volatitity :

They form hydrides of type H_2E (E-Grp 16 element) viz. H_2O, H_2S, H_2Se, H_2Te, H_2Po. 0 forms another imp hybride H_2O_2. The central atom of these hydrides are sp^3 hybridised and their geometry is angular.

Hydrides	H_2O	H_2S	H_2Se	H_2Te
H–E–H angle	104.5°	92°	91°	90°

H—bonding in H_2O



H-bonding in H_2O molecule is strong since electronegativity difference of H & O are high.

As we move from H_2S to H_2Po the strength of H-bonding goes on decreasing due to increase in size of the central atom and decrease in electronegativity.

Since O_2 is more electronegative the electron density around is maximum. Therefore, is H_2O the repulsion between electron pair is maximum. Hence H-O-H angle is maximum.

Water hydride of oxygen is a colourless, odouless liquid while the hydrides of all other elements of group are colourless, poisonous gases with unpleasant odour.

Volatility is in the order of $H_2O < H_2S > H_2Se > H_2Te$. Boiling point of H_2O is abnormally high and it is less volatile H_2S is most volatile. The abnormal boiling point and low volatility of water is due to association of H_2O molecules the intermolecular H-bonding.

Q. Why H_2S is a gas and H_2O a liquid ?

(ii) Thermal stability :

Thermal stability decreases as we move from H_2O to H_2Po due to increase in size of central atom as a result of which tendency to form E-H bond decreases.

(iii) Acidic characters :

It is tendency to donate $H^{\oplus}$ ions. As we move from H_2O to H_2Po the acidic character goes on increasing. Water is less acidic. The hydrides react with bases to form two types of salts.

For e.g. H_2S reacts with NaOH as follows :

$$H_2S + NaOH \longrightarrow \underset{\text{(Sodium hydrosulphide)}}{NaHS} + H_2O$$

$$NaHS + NaOH \longrightarrow \underset{\text{(Sodium sulphide)}}{Na_2S + H_2O}$$

Due to decrease in dissociation enthalpy of bond E–H down the group acidic character increases.

Q. H_2S is less acidic than H_2Te why?

E-H bonds percent in these hydrides are polar and dissociates is aqueous solution to produce H^+ ions which combines with H_2O molecules forming H_3O^+ ion. Hence these hydrides act as acids.

(iv) Reducing character :

It is ability to behave as reducing agent i.e. tendency to loose hydrogen.

Reducing character depends on thermal stability. Lesser is the thermal stability, greater is the reducing power of the hydrides. Reducing character increases from H_2O to H_2Po.

H_2Po is strongest reducing agent H_2O cannot behave as reducing agent due to presence of H-bonding as a result of which H_2O is stable.

(v) Reactivity to words Halogen :

The compounds of oxygen with flororine are called fluorides because F is more electronegative than O. Oxygen shows +ve oxidation state with fluorides e.g. OF_2, O_2F_2 while with other Halides shows –ve oxidation state e.g. Cl_2O_7.

The order of reactivity is $F^- > Cl^- > Br^- > I^-$. Amongst hexahalides hexa fluorides are only stable hexahalides SF_6 is stable.

The central atom present in SF_6 is in a state of sp^3d^2 hybridisation. It has octahedral geometry. Among tetrahalides SF_4 is a gas, SeF_4 is liquid while TeF_4 is solid having sp^3d hybridisation with trigonal biplaner geometry.

Q.3.T.B. Explain Amomalous behaviour of oxygen

Anomalous behaviour of oxygen :

The anomolous nature of oxygen is due to

(i) its small size.

(ii) Its high electronegativity

(iii) The absence of vacant d-orbitals in its valence shell

Some important points of difference are :

(1) Physical state : Oxygen is a gas at ordinary temperature while other members are solids.

(2) **Atomicity :** Oxygen molecule is diatomic (O_2) while molecule of other elements of group 16 are poly atomic.

Ex. Sulphur and selenium form octatomic molecules (S_8 and Se_8) have ring structure.

(3) **Oxidation state :**

Oxygen shows an oxidation state of –2 in most of its compounds. Due to absence of d-orbital it cannot exhibit higher oxidation state. The other elements of the group exhibit +2, +4 and +6 oxidation states in addition to –2 oxidation state.

(4) **Magnetic behaviour :** Molecular oxygen (O_2) is paramagnetic in nature while other elements are diamagnetic.

(5) **Hydrogen bonding :** Due to higher value of electronegativity, oxygen is capable of forming hydrogen bonding in its compound like water, alcohols, etc. other element of group being less electronegative do not form hydrogen bonds.

(6) **Nature of compounds :** The compound of oxygen are more ionic than those of the other elements of the group.

Thus O^{2-} is very common but S^{2-}, Se^{2-} & Te^{2-} are less common.

(7) **Hydrides :** The hydrides of oxygen i.e. H_2O is a liquid at room temperature while the hydrides of all other elements are gases.

Dioxygen :

Almost all the oxygen in the atmosphere is probably due its pholosynthesis by green plants. It is a very complicated process. It can be represented as

$$xH_2O + xCO_2 \xrightarrow{\text{sun light}} \underset{\text{carbohydrate}}{(CH_2O)_x} + XO_2(g)$$

* **PREPARATION**

* **General method**

(a) By the thermal decomposition of certain oxygen rich salts (Chlorates, nitrates etc.)

(i) $2KClO_3 \xrightarrow[MnO_2]{\text{heat}} 2KCl + 3O_2$

(ii) $2KNO_3 \xrightarrow{\text{heat}} 2KNO_2 + O_2$

(iii) $2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$

(iv) $2K_2Cr_2O_7 \xrightarrow{\text{heat}} 2K_2O + 2Cr_2O_3 + 3O_2$

(v) $2K_2Cr_2O_7 \xrightarrow{\text{heat}} 2K_2O + 2Cr_2O_3 + 3O_2$

Q33.T.B. How is oxygen prepared by thermal decomposition of certain metallic oxides.

(b) The thermal decomposition of metallic oxides

(i) $2HgO(s) \xrightarrow{720\text{ K}} 2Hg + O_{2(g)}$

(ii) $2Ag_2O(s) \xrightarrow{620\text{ K}} 4Ag + O_{2(g)}$

(iii) $2Ag_2O(s) \xrightarrow{620\text{ K}} 4Ag + O_{2(g)}$

(iv) $2PbO_{2(s)} \xrightarrow{heat} 2PbO_{(s)} + O_{2(g)}$

(v) $\underset{\text{Barium per oxide}}{2BaO_2} \xrightarrow{heat} 2BaO + O_2$

(vi) $2H_2O_2 \xrightarrow{heat} 2H_2O + O_2$

(vii) $6MnO_2 \xrightarrow{heat} 2Mn_3O_4 + O_2$

(c) By the action of water or acidified potassium permaganate on sodium peroxide :

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

$$2KMnO_4 + 5Na_2O_2 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 8H_2O + 5O_2$$

(d) Laboratary Method : Dioxygen can be prepared very conveniently by heating a mixture of $KClO_3$ (4 parts) and (MnO_2 (⊥ parts) in a hard glass tube to about 420K. The gas produced may be collected by the dowards displacement of water.

$$2KClO_3 \xrightarrow[MnO_7]{420K} 2Ka + 3O_2$$

when MnO_2 is absent, then temperature of 670 K – 72 K is required.

(e) Manufacture of O_2 : Commercial preparation of O_2 is done in two parts.

(i) From water : Electrolysis of acidified water gives H_2 at cathode and O_2 at the anode, Hence at places where electricity is cheap it is used.

(ii) From air : In large scale it is prepared by the fractional distillation of liquid air. The constituents of liquid air are liquid dinitrogen and liquid dioxygen. On distillation liquid dinitrogen distil out.

* **Properties of dioxygen :**

(i) It is colourless, tasteless and odourless gas.

(ii) Solubility in water is 30 cm^3L^{-1} at 293 K (S.T.P.). Dioxgyen dissolved in water is responsible for sustaining the life of animals in water.

(iii) Can be absorbed to a considerable extent in alkali pyrogallol.

(iv) Can be liquified to pale blue liquid (B.P. 20.2 K) can be solidified into a light blue solid (M.P. 54.4 K)

(v) It is heavier than air.

(vi) Paramagnetic in nature

(vii) Oxygen has three stable isotopes ^{10}O, ^{17}O, ^{18}O.

* **Chemical properties**

The reactions of oxygen requires initiation by external heating. At higher temperature it dissociates and combines with larger number of element and shows a variety of oxidation reaction.

1. Supporte of combustion : Dioxygen is not combustible but supports combustion.

2. Reaction with metals : Differents metals combine with oxygen to give their oxides.

(a) Active metal react at ordinary temperature and form their oxides.

(i) $2Ca + O_2 \longrightarrow 2CaO$

(ii) $4Na + O_2 \longrightarrow 2Na_2O$ (sodium oxide)

(b) Magnesium drums in dioxygen to give MgO

$2Mg + O_2 \longrightarrow 2MgO$

(c) Metals like Al, Fe, etc. combine with dioxygen on heating to form their oxide

(i) $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

(ii) $4Al + 3O_2 \rightarrow 2Al_2O_3$

(d) Non-metals turns lightly in dioxygen and forms their oxides

(i) $S + O_2 \rightarrow SO_2$

(ii) $P_4 + 5O_2 \rightarrow p_4O_{10}$

(iii) $\underset{(tinited)}{2C + O_2} \rightarrow 2CO$

(iv) $\underset{(excess)}{C + O_2} \rightarrow CO_2$

(v) $2H_2O + O_2 \xrightarrow{\Delta} 2H_2O$

(vi) $N_2 + O_2 \longrightarrow \underset{\text{Nitric oxide}}{2NO}$

(e) **Reaction with compounds :**

(i) **Reaction with ammonia** : It oxidises ammonia to nitric oxide in presence of red hot platinum

$$4NH_3 + 5O_2 \xrightarrow[\text{Pt}]{1073\text{ K}} 4NO + 6H_2O$$

(ii) **Reaction with sulphur dioxide :** It oxides sulphur dioxide into sulphur trioxide (SO_3) at 752 K is presence of finely divided platinum

$2SO_2 + O_2 \xrightarrow[\text{Pt}]{725\text{ K}} 2SO_3$

(iii) Reaction with hydrogen chloride : It oxidides hydrogen chloride gas into chlorine gas to 700 K in presence of cupric chloride as a catalyst

$4HCl_{(g)} + \underset{(g)}{O_2} \xrightarrow[CuCl_2]{700\text{ K}} 2H_2O_{(g)} + 2Cl_{2(g)}$

(iv) Reaction with carbon disulphide : Carbon disulphide burns in oxygen to form carbon dioxide and sulphur dioxide

$CS_2 + SO_2 \rightarrow 2SO_2 + CO_2$

(v) Reaction with metal sulphide : Metal sulphides such as ZnS, HgS, CuS etc reacts with dioxygen at high temperature to form their respective oxide and sulphur dioxide.

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$2MgS + 3O_2 \rightarrow 2MgO + 2SO_2$

(vi) Reaction with hydrocarbon : All saturated unsturated and aromatic hydro carbon atoms burn in excess of dioxygen (or in air) to form carbon dioxide and water

$$\underset{\text{Benzene}}{C_6H_6} + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O$$

$$\underset{\text{Methane}}{CH_4} + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$\underset{\text{Ethylene}}{C_2H_4} + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$$\underset{\text{Ethane}}{C_2H_6} + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

All these reaction are highly exothermic. Therefore hydrocarbons are used as fuels.

Uses of dioxygen :

(i) Dioxygen is essential for sustaining life. It is used by all living lungs in resparation. Mineus, deep sea arivers, firemen and auiatous are produced with oxygen cylinder. Also used in hospital for artificial respiration.

(ii) Liquid dioxygen is an important constituent or rocket fuel.

(iii) It is used in making oxy-hydrogen and oxy-acetylene torch which are used for cutting and welding of metals.

(iv) Mixture of powdered charcoal and liquid oxygen is used as an explosure in coal mining.

(v) It is used in metallurgical processes for remoring the impurities of metals by oxidation.

(vi) It is used in the manufacture of large number of compounds such as phenol, sulphuric acid and nitric acid.

CLASSIFICATION OF OXIDES :

Oxygen combines with a large number of metals and non-metals to form binary compounds. These binary compounds are called oxides.

Example :

(i) Carbon forms monoxide as CO

(ii) Carbon forms dioxide as CO_2

Q.34 T.B: What are different types of oxides? Give examples oxides are classified as acidic oxides, basic oxides and amphoteric oxides.

(1) Acidic oxides :

- Acidic oxides reacts with water to form Acidic solution.
- Acidic oxides are non-metallic oxides.
- Acidic oxides forms covalent bond

(i) $CO_{2(g)} + H_2O_{(l)} \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$

(ii) $N_2O_{5(g)} + H_2O_{(l)} \longrightarrow \underset{\text{Nitric acid}}{2HNO_{3(aq)}}$

(iii) $P_4O_{10(s)} + 6H_2O_{(l)} \longrightarrow \underset{\text{Phosphoric acid}}{4H_3PO_{4(aq)}}$

(iv) $SO_3 + H_2O \longrightarrow \underset{\text{Sulphuric acid}}{H_2SO_4}$

(2) Basic oxides :

* Basic oxides reacts with water to form Basic solution.

* Basic oxides are metallic oxides.

* Basic oxides forms ionic bond

(i) $CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$

(ii) $MgO + H_2O \longrightarrow Mg(OH)_2$

(3) Amphoteric oxides :

* Amphoteric oxides shows character of both Acidic as well as Basic i.e. they reacts with both acids & bases.

$$Al_2O_3 + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$$

$$ZnO_{(aq)} + \underset{\text{(excess)}}{2NaOH} \longrightarrow Na_2ZnO_{2(aq)} + H_2O_{(l)}$$

$$ZnO_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_2O_{(l)}$$

(4) Neutral oxides :

* Neutral oxides are neither acidic nor basic.
Examples : N_2O, NO, CO

* Ozone (O_3) [Allotropic form of oxygen]

(I) Two methods for preparation of ozone

(i) Natural method

(ii) Artificial method

(i) Natural method :

Step : (a) Naturally, ozone is formed in the atmosphere through photochemical reaction.

Oxygen absorbs the Sun's radiation to produce one ground state and other excited state (0*) oxygen atoms.

$$O_2 \xrightarrow[175\text{ nm}]{h\nu} O + O^*$$

Step : (b) The excited oxygen atom (O*) being unstable, deactivated by collision with another oxygen molecule to give single molecular oxygen.

$$O^* + O_2 \longrightarrow O + O_2$$

Step : (c) Finally, the ground state oxygen combines with oxygen molecule to form ozone in the excited state and that excited state is stabilized by the 3rd body by various ways.

$$O + O_2 \longrightarrow O_3^*$$

$$O_3^* + M \longrightarrow O_3 + M$$

M can be O_2 or N_2 or any inert molecule which removes excess energy of recombination than can stop decomposition of O_3.

(ii) Artificial or Laboratary preparation :

When an electrical discharge is through in oxygen, it gets converted to ozone (about 10%). The product is known as ozonized oxygen.

(II) Properties :

1. Gaseous ozone is blue, liquid ozone is bluish black and solid ozone is violet black or blackish violet.
2. It has pungent smell.
3. In small concentration it is non-toxic other wise in high concentration (100 ppm) it is toxic

Q.33. (T.b)

Ans. (i) It oxidises sulphides to sulphates, ideal sulphide oxidizes to lead sulphate

$$PbS_{(s)} + 4O_{3(g)} \longrightarrow PbSO_{4(s)} + 4O_{2(g)}$$

(ii) Iodine gets liberated from neutral postassium iodide solution.

$$2KI_{(aq)} + H_2O + O_{3(g)} \longrightarrow 3KOH_{(aq)} + I_{2(s)} + O_{2(g)}$$

$\therefore$ Ozone is oxiding agent.

(5) It also behaves as a reducing agent when treated with BaO_2 and H_2O_2

(i) $BaO_2 + O_3 \longrightarrow BaO + 2O_2$

(ii) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

$\therefore$ O_3 is reducing agent

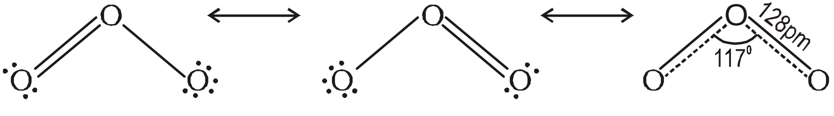
Q.39. (T.B) How is ozone estimated :

(6) Estimation of ozone : Ozone when treated with excess of potassium iodide solution containing borate buffor liberates iodine. The librated iodine is titrated against sodium thiosulphate, to determine ozone quantitatively.

(7) Aircraft engine emitis exhaust gas contains nitrogen oxide (NO) which combines with O_3 and results in depletion of ozone. $NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$

(III) Structure of zone :

Ozone is angular with O – O – O bonds angle as 117°. Both O – O bonds are identical. Bond length is 128 pm which is intermediate between single and double bonds has 2 resonances hybrid structures.



Resonating structures

(IV) Uses :

Q.35(T.B)Explain : Protective umbrell as zone for UV from sun.

Ans.(i) Ozone absorbs light energy strongly in the region 220–290 cm of the specturm. Thus it prevents the harmful ultroviolet rays of the sum from reaching the earth's surface.

(ii) It has bleaching properties

(iii) It is used as disinfectant and germicide

(iv) It is used for sterlization of air and water.

Sulphure :

Q.4.OT.B. Occurence of sulphure :

Sulphur occurs in native state (free state) as well as in the combined state. In the combined state it manly occurs as :

(i) Sulphide : Sulphur is widely distributed as sulphides of metals, e.g. copper pyrites (Cu_2S), from pyectes (Fe_2S_2), Zinc blende (ZnS), ainabar (HgS), galena (PbS) etc.

(ii) Sulphates : A large quantity of sulphur is distributed as sulphate in nature e.g. ggpsum, ($CaSO_4.2H_2O$), epsum ($MgSO_4$, $7H_2O$), lwytes ($BaSO_4$), Glauber's salt (Na_2SO_4, $10H_2O$) etc.

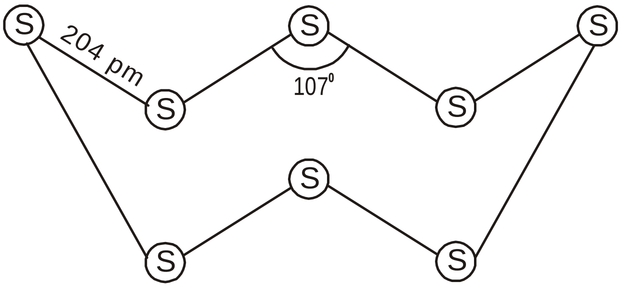
Q.28 T.B. What are alltropic forms of sulphur?

* **Allotropic forms of sulphur :**

Sulphur exhibits the phenomenon of allotropy and exits is raibous allotropic forms. The following are the important forms of sulphur.

(i) Rhomic sulphur :

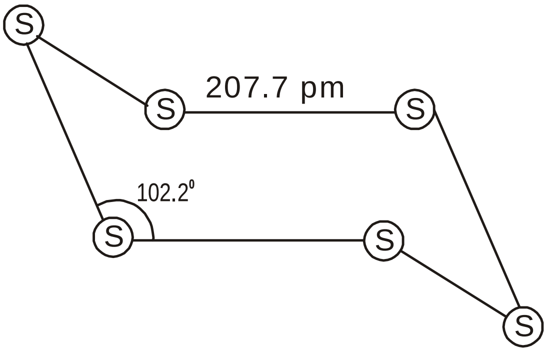
- ☛ This is the most common and most state form of sulphur.
- ☛ It is also called α–sulphur or onctahedral sulphur.
- ☛ It is pale yellow in colour. It has specific gravity of 2.06.
- ☛ Its m.p. is 385.8 K
- ☛ It is insoluble in water but soluble in carbon disulphide.
- ☛ This form is stable at room temperature.
- ☛ Rhombic sulphur is found to consist of S_8 units at room temperature. The eight sulphur atoms present in a molecule form a puckred ring in a carbon shpae.



(a) Crown structure of sulphur

(ii) Maxoclinic sulphur :

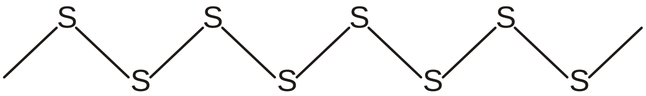
- It is also called β-sulphur or puismatic sulphur.
- Its m.p. is 393 K and specific gravity 1.98.
- It dissolves in CS_2
- It is stable above 369 K and gets converted into α-sulphur below 369 K.
- At 369 K both the forms, α and β sulphur are stable.
- Monoclinic sulphur also exists as S_8 molecules which possess a puckered ring structure similar to α-sulphur. It is obtained by melting the sulphur and cooling till crust is formed
- On removing the crust, the transparent crystals of monoclinic sulphur are formed, which are needle shaped.
- In cyclo-S_6, the ring has chair form and the molecular dimensions are shown.
- Small S_n molecules are unstable and exist in sulphur vapours are S_2 and S_3 molecules.
- S_2 molecule which has two unpaired electrons in the antibonding orbitals like O_2 and hence shows paramgnetism.
- S_8 is cherry red in colour like ozone and S_2 is violet in colour like O_2.



(b) Chair structure of sulphur

(iii) Plastic sulphur (Sy) :

* It is also called g–sulphur
* Elastic sulphur consists of an open chain structure.
* Its specific gravity is 1.95.
* It is soluble neither in water nor in carbon disulphide.
* It is a soft rubber like amorphous mars.
* It possess no shapr melting point



Open chain S_8 molecule

(iv) Milk of sulphur :

When flowers of sulphur are boiled with milk of line, a mixture of calcium pentasulphide (CaS_5) and calcium thiosulphur (CaS_2O_3) is formed. This mixture on being treated with hydrochloric acid gives a white amorphus precipitate known as milk of sulphur.

$$3Ca(OH)_2 + 12S \longrightarrow \underset{\text{(Calcium pentasulphide)}}{2CaS_5} + \underset{\text{(Calcium thiosulphate)}}{CaS_2O_3} + 3H_2O$$

$$2CaS_5 + CaS_2O_3 + 6HCl \longrightarrow 3CaCl_2 + 3H_2O + \underset{\text{Milk of sulphur}}{12S}$$

Milk of sulphur is soluble in CS_2. It tends to revert to the rhombic variety on standing for long time. It is used is medicine.

(v) Colloidal sulphur : Colloidal form of sulphur may be obtained by passing hydrogen sulphide through nitric acid or by treating sodium thiosulphate solution with concentrated hydrochloric acid.

$$H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + \underset{\text{Colloidal sulphur}}{S}$$

$$Na_2S_2O_3 + \underset{\text{(Conc.)}}{2HCl} \longrightarrow 2NaCl + SO_2 + H_2O + \underset{\text{Colloidal sulphur}}{S}$$

It may lu obtained by treating hydrogen sulphides with sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 2H_2O + \underset{\text{Colloidal sulphur}}{3S}$$

Variety of colours of colloidal sulphur are obtained, depending upon size of the sulphur particles.

* **Compounds of sulphur :**

(a) Sulphur dioxide :

Preparation :

It occurs in volcanic gases and by burning of coal.

(1) SO_2 is formed when sulphur is **????** in iar, or oxygen. Some amount of SO_3 is also formed along with SO_2.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

(2) Laboratory methods :

(i) Action of concentrated sulphuric acid on copper farming

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

(ii) It is readily obtained by teating sodium sulphite with dilute hydrochloric acid.

$$Na_2SO_{3(aq)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + SO_{2(g)}$$

Q.41. How SO_2 is manufacture?

(i) Industrial method :

It is produced as a by product of the roasting of pyrites and belendes

$$4FeS_{2(s)} + 11O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

The gas is dried liquified under pressure and stored in stell cylinders.

* **Properties :**

(i) Sulphur dioxide is colourless gas, acidic in nature and having pungent and suffocating smell.

ii) It is highly soluble in water

If forms H_2SO_3 . ($SO_2 + H_2O \longrightarrow H_2SO_3$) and also called anhydride of sulphurous acid.

(iii) It liquifies at room temperature under a pressure of 2 atm and boils at 263 K.

(iv) It acts as a strong reducing agent and reduces

(a) Halogens to halogen acid.

$$I_2 + SO_2 + 2H_2O \longrightarrow 2HI + H_2SO_4$$

(b) Turns acidified $K_2Cr_2O_7$ solution green

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

(v) Its reacts with sodium hydroxide solution, forming sodium sulphite which further reacts with more sulphur dioxide to form sodium hydrogen sulphite.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

(vi) SO_2 combines with chlorine in the presence of charcoal as a catalyst to produce SO_2Cl_2 (sulphuryl chloride). SO_2 is gets oxidized to SO_3 by oxygen in the presence of V_2 of as catalyst.

$$SO_{2(g)} + Cl_{2(g)} \longrightarrow SO_2Cl_{2(l)}$$

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$$

(vii) It convert Fe(III) to Fe(II) and decolourless acidified $KMnO_4$ (Mn is VII state). In this Mn(VII) changes to Mn(II).

$$2FeCl_3 + SO_2 + 2H_2O \longrightarrow 2FeCl_2 + H_2SO_4 + 2HCl$$

$$5SO_2 + 2KMnO_4 + 2H_2O \longrightarrow K_2SO_4 + zMnSO_4 + 2H_2SO_4$$

(viii) It acts as oxidizing agent and a Lewis base. For example, it oxidized H_2S to S and ferrous chloride to ferric chloride.

$$2H_2S + SO_2 \longrightarrow 2H_2O + S3\downarrow$$

$$4FeCl_2 + SO_2 + 4HCl \longrightarrow 4FeCl_3 + 2H_2O + 8S$$

* **Uses :**

* Sulphur dioxide is used in manufacture of H_2SO_4.

* It is also used in the defining of petrollum and **????** industry.

* For fumigation, as a germicide and preseving of fruits.

* As an anti disinfectant and preservative.

* Liquid SO_2 is used as solvent to dissolve many inorganic and organic compounds.

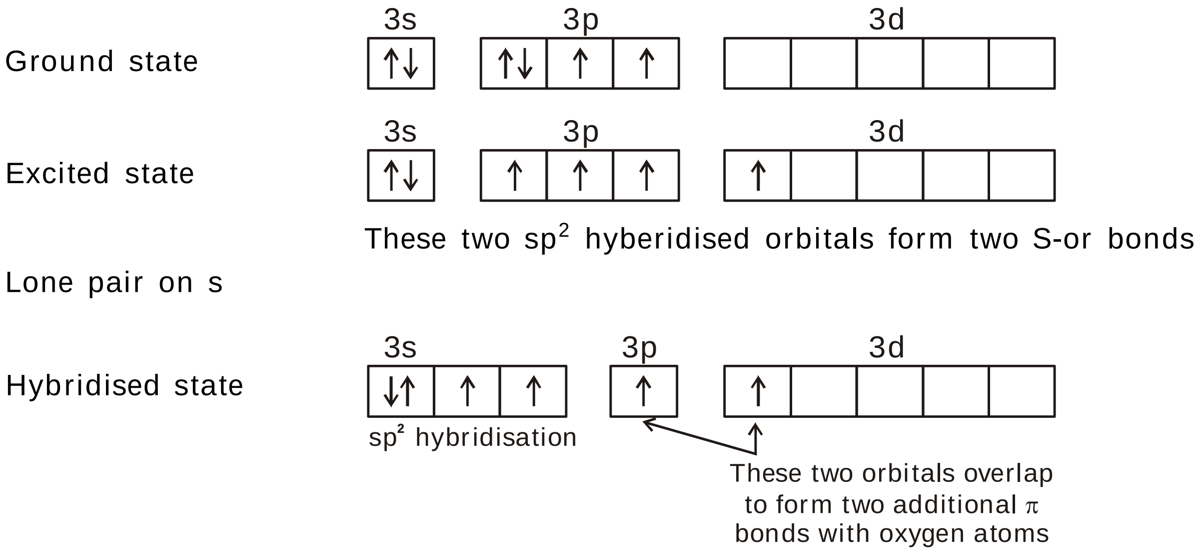
* It is used as bleaching agent in the presence of moisture.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2(H)$$

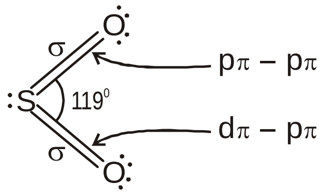
- It acts as Lewis base due to presence of lone pair of electrons on sulphur atom.

Q.42. Explain :

- **Structure of SO_2 molecules :**
  - The molecule of SO_2 has a bent structure with a O-S-O bond angle of 119º, sulphur is sp^2 hybridised and the lone pair of electrons of sulphur reduces the angle from 120ºC to 119º.
  - In the structure each oxygen atom is joined to sulphur by a σ and π bond.
  - The σ bonds between S and O are formed by sp2-p overlap while one of the π bonds arises from $p\pi - p\pi$ overlap and other from $p\pi - p\pi$ overlap but even both of the S-O bonds are identical due to resonance.



(a) Hybridisation of s in SO_2 molecule



- **Sulphuric acid :**

  It is important chemical used in many industries. It is also called as oil of vitroil in ancient days. There are to manufacturing process : a) contact process b) lead chamber process

Q.43.T.B.(A) Contact process :

(a) Preparation of SO_2 : $S_{(g)} + O_{2(g)} \longrightarrow SO_{2(g)}$

(b) Oxidation of SO_2 to SO_3 :

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_3 \qquad \Delta H = -196.6 \text{ KJ}$$

The optimum pressure used is 2-3 atom.

As the forward reaction is exothermic it is favoured at low temperature, optinum temperature used in around 723 K and SO_2 and O_2 are taken in the ratio 2 : 3.

(c) Dissolution of SO_2 in H_2SO_4 :

SO_3 is absorbed in 98% H_2SO_4 to get $H_2S_2O_7$, oleum.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

SO_3 is not dissolved in water as it forms adense fog.

(d) Dilution of oleum : $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

H_2SO_4 obtained by this process is 96-98%.

(B) Lead chamber process :

In this process a mixture of SO_2, NO and air is treated with steam to obtain H_2SO_4. NO acts as catalyst.

Preparation of SO_2 :

$S + O_2 \longrightarrow SO_2$ (oxidation of sulphur)

Preparation of SO_3 :

$$2HNO_3 + 2SO_2 \longrightarrow H_2O + NO + 2SO_3$$

Nitric acid or NO_2 is used to oxidize SO_2 to SO_3.

OR $SO_2 + NO_2 \longrightarrow SO_3 + NO$

Dissolution of SO_3 :

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Properties :

1. It is a colourless, dense, oily liquid.
2. It has specific gravity of 1.84 at 298 K.
3. It is a strong acid with powerful affinity for water, less volatile and acts as oxidizing agent.
4. It is highly viscous due to hydrogen bonding.
5. For the preparation of dil.H_2SO_4 solution from conc. H_2SO_4, the concentrated acid must always be added slowly into fine stream of water with constant stirring.
6. It is a dibasic acid :

(i) $H_2SO_4 \rightleftarrows H^+ + HSO_4^-$ $ka_1 > 10$

(ii) $HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$ $ka_2 = 1.2 \times 10^{-2}$

(iii) $HSO_4^- + H_2O \longrightarrow H_3O^+ + SO_4^{2-}$

Greater the value of dissociation constant (K_a) the stronger is the acid.

*** H_2SO_4 as dehydrating agent :**

Conc. H_2SO_4 is a powerful dehydrating agent. Its corrosive action on the skin is also due to dehydration of skin which then burns and develops itching sensation.

(a) $\underset{\text{formic acid}}{HCOOH} \xrightarrow{H_2SO_4} CO + H_2O$

(b) $\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{H_2SO_4} 6C + 6H_2O$

(c) $\underset{\text{oxalic acid}}{(COOH)_2} \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$

(d) $\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2SO_4} 12C + 11H_2O$

((e) $\underset{\text{Ethyl alcohol}}{2C_2H_5OH} \xrightarrow{H_2SO_4} \underset{\text{Ether}}{C_2H_5OC_2H_5} + H_2O$

* **Oxidizing property :**

* $H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$

Hot conc. H_2SO_4 acts as oxidizing agent.

* It oxidizes non metal carbon, sulphur, phosphorus

(i) $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

(ii) $S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$

(iii) $P_4 + 10H_2SO_4 \longrightarrow P_4O_{10} + 10SO_2 + 10H_2O$

(iv) $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

* H_2SO_4 oxidizes the metals above hydrogen in electronchemical series.

$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + 2H_2O + SO_2$

* Oxidation of metals below hydrogen in electrochemcial series.

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

* Halogen acids and ferrous sulphate are oxidized by sulphuric acid.

$2HX + H_2SO_4 \xrightarrow{heat} X_2 + SO_2 + 2H_2O$

(where x = Br or I)

$2FeSO_4 + 2H_2SO_4 \xrightarrow{heat} Fe_2(SO_4)_3 + SO_2 + 2H_2O$

$2HI + H_2SO_4 \longrightarrow 2H_2O + SO_2 + I_2$

* Action of dil. H_2SO_4 on metals :

$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_{2(g)}$

* It acts as a solphonating agent :

$C_6H_6 + HOSO_2OH \longrightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_2 . OH} + H_2O$

* Reaction with PCl_5 :

$HO.SO_2 . OH + PCl_5 \longrightarrow \underset{\text{(Chlorosulphuric acid)}}{ClSO_2OH} + POCl_3 + HCl$

$ClSO_2OH + PCl_5 \longrightarrow \underset{\text{(Sulphuryl chloride)}}{ClSO_2} + POCl_3 + HCl$

- Crystals of $[K_4Fe(CN)_6]$ when heated with conc. H_2SO_4, carbon monoxide is evolved.

$$[K_4Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

- Action of conc. H_2SO_4 on $KClO_3$ (Potassium chlorate)

$$3KClO_3 + 3H_2SO_4 \longrightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$$

- It forms hydrogen fluoride with CaF_2

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Q.44.T.B.

- **Uses of H_2SO_4 :**
  - (i) It is regarded as king of chemicals. It is used in the manufacture of dyes, fertilizers, detergents, explosives etc.
  - (ii) It is used in the preparation of HNO_3, HCl, H_3PO_4, Na_2CO_3, sulphates, alum, ether etc.
  - (iii) In lead storage batteries.

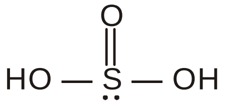
    $$PbO_2 + Pb + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$
  - (iv) It is commonly used as laboratory agent.
  - (v) It is dehydrating agent.
  - (vi) It works as oxidizing agent.
  - (vii) It is used in refining of petroleum.
  - (viii) It is used as a pickling agent.

Q.37. T.B. Explain and Draw structures of oxyacids of sulphuric.

- **Oxa acids of sulphur :**
  - (i) Sulphoxylic acid, H_2SO_2

    $H — O — S — OH$ (+2)

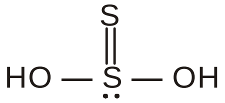
    Sulphorous acid series :
  - (ii)



$$HO - \overset{\overset{\displaystyle O}{\|}}{\underset{\cdot\cdot}{S}} - OH$$

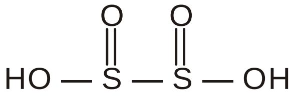
Sulphorous acid (+4) H_2SO_3

  - (iii) Thiosulphurous acid, $H_2S_2O_2$



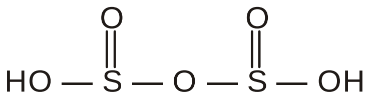
$$HO - \overset{\overset{\displaystyle S}{\|}}{\underset{\cdot\cdot}{S}} - OH \quad (-2, +4)$$

  - (iv) Dithionous acid, $(H_2S_2O_4)$



$$HO - \overset{\overset{\displaystyle O}{\|}}{S} - \overset{\overset{\displaystyle O}{\|}}{S} - OH \quad (+3)$$

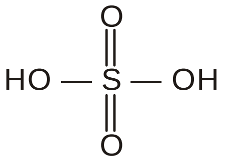
  - (v) Pyrosulphorus acid or dicolphorus acid, $H_2S_2O_5$



$$\mathrm{HO-\overset{\overset{O}{\|}}{S}-O-\overset{\overset{O}{\|}}{S}-OH}$$

(+4)

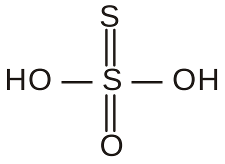
(vi) Sulphuric acid, (H_2SO_4)



$$\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$$

(+6)

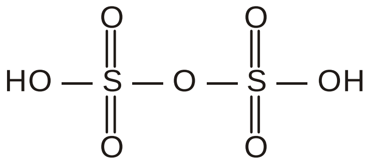
(vii) Thiosulphuric acid, ($H_2S_2O_3$)



$$\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{S}{\|}}{S}}-OH}$$

(–2, +6)

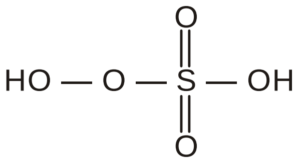
(viii) Pyrosulphuric acid or oleum, ($H_2S_2O_7$)



$$\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$$

(+6)

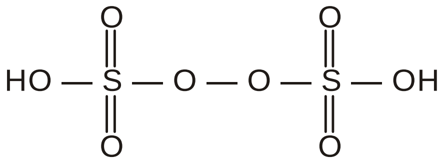
(ix) Peroxy monosulphuric acid, (H_2SO_5)



$$\mathrm{HO-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$$

(+6)

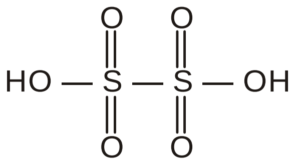
(x) Peroxy disulphuric acid, ($H_2S_2O_8$)



$$\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$$

(+6)

(xi) Dithionic acid, ($H_2S_2O_6$) (+5)



$$\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$$

(+5)

HYDROGEN CHLORIDE [HYDROCHLORIC ACID]

(I) Methods of preparation :

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

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

(II) Properties :

(i) It is a colourless gas with pungent odour.

(ii) It is highly soluble in water and ionizes, giving a strongly acidic solution.

$$HCl_{(g)} + H_2O_{(g)} \longrightarrow H_3O^{+}{}_{(aq)} + Cl^{-}$$

Ka = 10

Its aqueous solution is called hydrochloric acid.

(iii) Reaction with NH_3 to form white fumes

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

(i) $NaHSO_3 + HCl \longrightarrow NaCl + H_2O + SO_2$

(ii) $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$

(iii) $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

(iv) $CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

(v) $Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$

(vi) $NaOH + HCl \longrightarrow NaCl + H_2O$

(III) Uses of hydrogen chloride :

It is used :

(i) In the manufacture of chlorine and ammonium chloride.

(ii) To manufacture dye

(iii) To manufacture glucose from corn starch

(iv) In medicine and electroplating

(v) For the laboratory preparation of H_2 gas from metals.

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

When HCl reacts with finely powered iron, it forms ferous chloride.

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

* Interhalogen compounds : When two different halogens forms compounds among themselves, interhalogen compounds are formed.

Type : AA', AA'_3, AA'_5 and AA'_7

where A = halogen of large size less electronegativity.

A' = halogen of small size more electronegativity

E.g.

Type	Example :			
AA'	ClF,	BrF,	BrCl,	ICl
AA'_3	ClF_3	BrF_3,	IF_3,	ICl_3 (unstable)
AA'_5	IF_5,	BrF_5	ClF_5	
AA'_7	IF_7			

(I) Preparation :

(i) Formation of ClF (Chlorine Monofuloride), it is colourless gas

$$\underset{[\text{equal volume}]}{Cl_2 + F_2} \xrightarrow{473\,K} 2ClF$$

(ii) Formation of ClF_3 (Chlorine fluoride) - It is colourless gas.

$$Cl_2 + \underset{[\text{Excess}]}{3F_2} \xrightarrow{573\,K} 2ClF_3$$

(iii) Formation of ICl_3 – It is yellow powder. $I_2 + \underset{(\text{Excess})}{3Cl_2} \longrightarrow 2ICl_3$

(iv) Formation of BrF_3 – It is yellow green liquid. $\underset{(\text{dilute with water})}{Br_2 + 3F_2} \longrightarrow 2BrF_3$

(v) ICl formation - It is ruby red solid, α form and Brown red solid, β form.

$$\underset{(\text{Equimolar})}{I_2 + Cl_2} \longrightarrow 2ICl$$

(vi) Formation of BrF_5 - It is colourless liquid. $Br_2 + \underset{(\text{excess})}{5F_2} \longrightarrow 2BrF_5$

(II) Properties of interhalogen :

(i) Interhalogen compounds are covalent in nautre, due to the low electro negativity difference between halogen.

(ii) All these compounds are volatile and non-explosive.

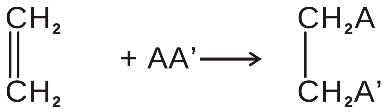
(iii) They are diamagnetic in nature.

(iv) They are more reactive than halogens. This is because $A - A'$ bonds present in them are weaker than

(v) They undergo hydrolysis with water $21F_5 + 5H_2O \longrightarrow 10HF + I_2O_5$

(vi) Interhalogens compounds of the type AA' form addition compounds with unsaturated hydrocarbons.

e.g.



$$CH_2{=}CH_2 + AA' \longrightarrow CH_2A{-}CH_2A'$$

Structure of interhalogen compounds.

(I) Type (1) : AA'

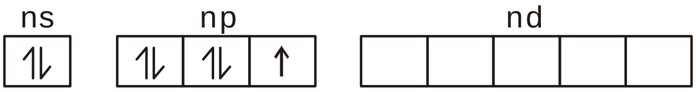
AA' are very simple and consists of two halogen atoms linked together through a single covalent bond. Thus their structure can be represented as $A - A'$. It is linear.

(II) Type (2) : AA'_3

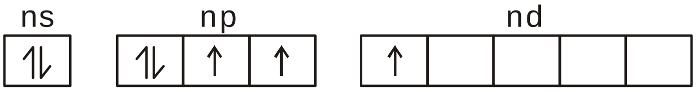
The expected structure of AA'_3 is T-shaped or bipyramidal structure.

- It is sp^{3}d hydridized.
- Central atom is eg. AF_3

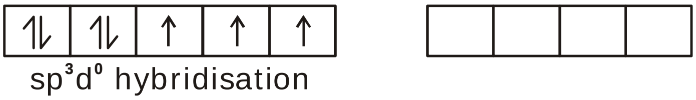
Group state



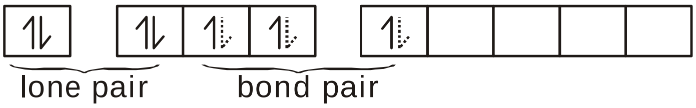
1st Excite state



Hydridized state

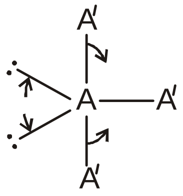


AA_3'

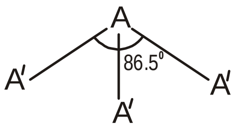


where ⇣ → electron of A'

Expected sp^{3}d hybridisation was tbp



Due to presence of two lone pair there is replusion and bond angle decreases from 90^o to 86.5^o and corresponding structure is 'Bent-T-shaped.

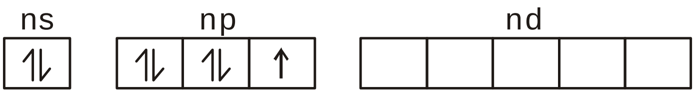


e.g. ClF_3, BrF_3, IF_3

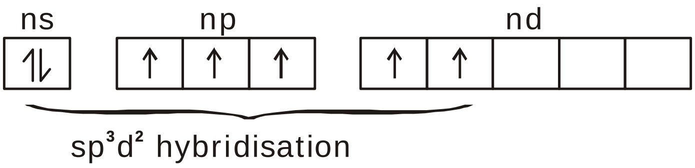
(III) Type (3) - AA_5'

The expected structure of AA_5' is octahedral central atom is which is sp^{3}d^2 hybridised (XF_5)

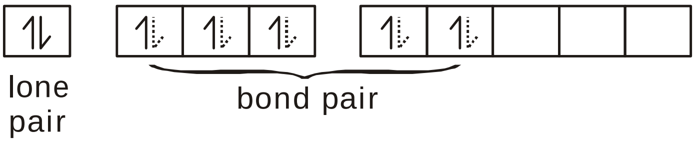
Ground state :



(Second excited state)

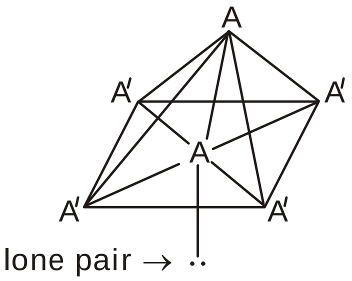


AA_5'



where ⇣ = electron of A'

Due to present of lone pair the octahedral [(i.e. Except structure)] distorded and square pyramid is obtained.



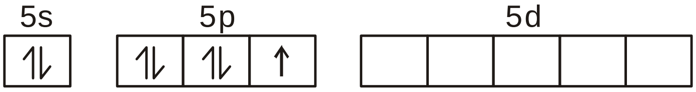
Square pyramid

(IV) Type (4) : AA'_7

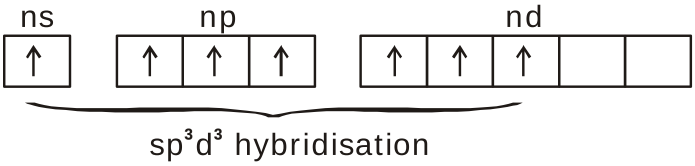
The only known interhalogen compounds of the type AA'_7 is IF_7

- * Central atom is A
- * Sp^3d^3 hybridization
- * Pentagonal bipyremidal structure

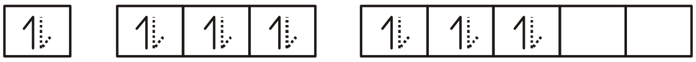
Ground state :



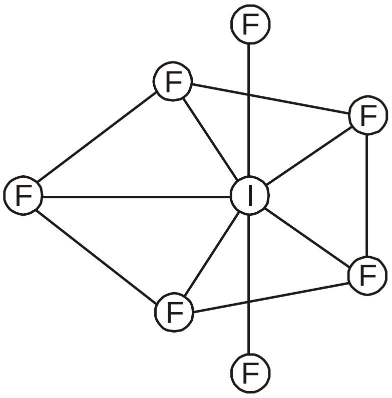
Third excite state :



IF_7 :



where ⇣ = electron of f



Uses of interhalogen :

(i) Interhalogen compounds of the type AA' are used as halogenating agent.

(ii) They are used for preparation of polyhalides.

(iii) ClF_3 and BrF_3 is used as oxidizes in propellants as well as fluorinating agent.

(iv) In production of UF_6.

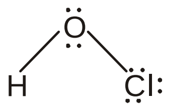
$U_{(S)} + 3ClF_{3(l)} \longrightarrow UF_{6(g)} + 3ClF_{(g)}$

* **Oxyacids or oxoacids of halogen :**

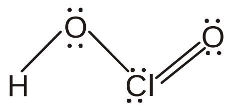
Fluorine forms only one oxyacid (i.e.) HOF hypoflurous acid. It is due to high electronegativity and small size.

Oxyacids of halogens	Hypohalous Acid	Halous acid	Halic acid	Perhalic acid
Fluoride	HOF Hypofluorous acid	–	–	–
Chlorine	HOI hypochlorus acid	HOClO chlorous acid	$HOClO_2$ chloric acid	$HOClO_3$ penchloric acid
Bromine	HOBr Hyprobromoul acid	–	$HOBrO_2$ Bromic acid	$HOBrO_3$ perbromic acids
Iodine	HOI Hypoiodous acid	–	$HOIO_2$ Iodic acid	$HOIO_3$ periodic acid

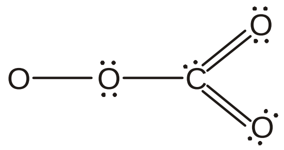
STRUCTURE OF OXYACIDS OF CHLORINE :



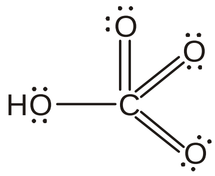
HOCl
[Oxidation state + 1]



HOClO
[Oxidation state + 3]



$HOClO_2$
[Oxidation state + 5]



$HOClO_3$
[Oxidation state + 7]

Oxiding Power of these oxyacids decreases as the oxidation number of halogen increases

$HClO > HClO_2 > HClO_3 > HClO_4$

Thermal stability increase in oxidation state of halogen

$HClO < HOClO < HOClO_2 < HOClO_3$

GROUP - 17

Electric configuration of group 17 elements

Element	Symbol	Atomic no.	Valence shell electronic
Fluorine	F	9	$2s^2 2p^5$
Chlorine	Cl	17	$3s^2 3p^5$
Bromine	Br	35	$4s^2 4p^5$
Iodine	I	53	$5s^2 5p^5$
Astatine	At	85	$6s^2 6p^5$

Physical trends (Properties)

1. **Physical state :**

   Fluorine and chlorine are gases at room temperature bromine is a liquid while iodine is a solid.

   In the elemental state all the halogens exist as diatomic molecules.

2. **Atomic size :**

   The atomic size of Fluorine is the smallest in the period. The atomic size increase on moving down the group.

   Thus, the atomic size of Astatine is the largest due to addition of a new electronic configuration to it.

   Q.46. T.B.

3. **Electronegativity :** Halogen (Fluorine) possess Very high values of electronegativity. In fact each halogen is the most electronegative element of its period.

   The electronegativity values decrease on moving down the group.

   Hence, electronegavity values decreases from F to I. Fluorine is most electronegative element.

   Q.46.T.B. Ionization onthalpy :

4. The ionization enthalpies of halogens are very high. The ionization enthalpies decrease on moving down the group. The high ionization enthalpies are due to their small atomic size and high electronegativity charge.

   Fluorine atom is the smallest its ionization enthalpy is the highest and has no tendency to lose electrons.

   While Iodine atom is the highest so its ionization enthalpy is the lowest and has a tendency to form I^+ ions by losing one electron.

5. **Electron gain enthalpy :**

   Electron gain enthalpy of Fluorine is less than that of chlorine due to smaller atomic size of fluorine due to which incoming electron experiences a force of repulsion due to whichless amount of energy is released.

   As we more from Cl-I the electronegativity decreases.

6. **Non metallic character :**

   Due to higher values of electronegativity, Fluorine are non-metals. Non metallic character decreases down the group so Iodine shows metallic properties.

7. **Density :**

The density of halogens increases on moving down the group. This is due to an increase in the state of agglomerisation (tendency of atoms to come closer)

8. Melting point and Boiling point :

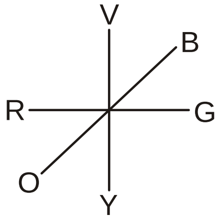
As we move from Fluorine to Iodine its Agglomerisation increase and due to this its melting point and Boiling point also increases.

9. Colour :

All halogenes are coloured. They show an interesting variation in colours from Yellow (Fluorine) Greenish yellow (chlorine) through reddish brown (Bromine) to violet (iodine). This is due to absorption of energy from Visible light. We know energy is related to wavelength which is related to visible region which is coloured. (VIBGYOR).

Therefore, Fluorine absorbs high energy (Violet light) and emits low energy (yellow light) while Iodine absorbs low energy (yellow light) and emits high energy violet light.

NOTE :



10. Oxidation state :

Fluorine is most electronegative element and hence it shows only (–1) oxidation state due to small atomic size, higher electronegativity and Absence of d-orbitals.

Although the general oxidation state of group-17 element is –1.

However Cl, Br, I due to presence of vacant d-orbital shows oxidation states like +1, +3, +5, +7.

Also +4 & +6 oxidation states are shown by Cl and Br in compounds like ClO_2, BrO_3 etc.

1. Oxidizing nature :

This is the tendency to behave as an oxidizing agent i.e. gain of $e^{(-)}s$. The oxidizing power of halogens decreases from flourine to iodine. Thus fluorine is the strongest oxidizing agent. Fluorine can displace chlorine, bromine and iodine. Chlorine can displace bromine and iodine while bromine displaces iodine.

2. Reaction with metals and non-metals :

The reactivity decreases as we go down the group from fluorine to iodine. For example with sulphur fluorine forms hexa-fluoricle (SF_6) chlorine forms tetrachloride (SCl'_4) bromine forms dibromide (Br_2) and iodine does not react at all. The order of strength of band is

M–F > M–Cl > M–Br > M–I

3. Reactivity towards hydrogen :

All halogens react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. The acidic strength of there acids vary in the order.

HF < HCl < HBr < HI

The electronegativity difference for fluorine is high due to the presence of hydrogen bonding. The presence of intermolecular hydrogen bonding leads to association of HF molecules as shown below

$$\ldots\ldots \overset{\delta+}{H} - \overset{\delta-}{F} \ldots\ldots\ldots \overset{\delta+}{H} - \overset{\delta-}{F} \ldots\ldots\ldots \overset{\delta+}{H} - \overset{\delta-}{F}$$

Therefore HF exists as liquid while HCl as gas.

Thermal stability : The thermal stability decreases HF to HI.

4. **Reducing character :** The reducing character increases from HF to HF to HI.

5. **Acidic character :** The acidic character increases from HF to HI.

6. **Reaction with water :**

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

$X_2 + H_2O \longrightarrow WX + HOX$ where X = Cl or Br

$$I^- + O_2 + H^+ \longrightarrow I_2 + H_2O$$

7. **Reaction with hydrocarbons :**

All the halogens react with hydrocarbons but the reactivity decreases with increase in atomic number.

$$F_2 + CH_4 \longrightarrow C + HF$$

$$Cl_2 + CH_4 \longrightarrow CCl_4 + HCl$$

8. **Reaction with alkali :**

Fluorine react with alkali giving fluorides, oxygen and water.

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

The other halogens react with cold NaOH solution to form halides and hypohalides.

$$\underset{\text{(cold)}}{2NaOH} + Cl_2 \longrightarrow NaCl + \underset{\text{Hypochlorite}}{NaOCl} + H_2O$$

With hot NaOH solution, hypochlorite breaks up and forms chloride and chlorate.

$$\underset{\text{(hat)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + \underset{\text{sodium chlorate}}{NaClO_3} + 3H_2O$$

9. **Bleaching agent :**

Fluorine and iodine does not show bleaching action. Moist chlorine is a good bleaching agent where as moist bromine shows slow bleaching action.

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

$$HOCl \longrightarrow HCl + [O]$$

* **Anamalous behaviour of fluorine :**

Fluorine exhibits anamalous behaviour due to :

(i) Its small size

(ii) Highest electronegativity

(iii) Absence of d-orbitals

The main points of difference between fluorine and other elements of group 17 are as follows :

1. **Hydrogen bonding :**

Due to small atomic size and high electronegativity, fluorine forms hydrogen bonding in its hydrides. Other elements do not form hydrogen bonding.

2. **Behaviour of HF :**

   Due to presence of hydrogen bonding the behaviour of hydrofluoric acid is different that of other halogen acids.

   (i) Hydrofluoric acid is a liquid while other acids are gases.

   (ii) Hydrofluorine acid is a weak acid while other halogen acids are strong acids.

3. **Oxidation state :** Fluorine exhibits only –1 oxidation state in all its compounds. When elements of the group exhibits +1, +3, +5, +2 and +7 oxidation states.

4. **Nature of compounds :** As fluorine has the highest electronegativity, it has strong tendency to form ionic compounds. All other elements form covalent compounds as well as ionic compounds.

5. **Polyhalide ions :** Fluorine does not form any polyhalide ion where as other halogen form polyhalide ions.

COMPOUNDS OF HALOGEN :

Chlorine - It is discovered by Schule in 1774. Later on Davy suggested the name chlorine on accounts of its colour.

1. **Occurence :**

   Chlorine does not occur in free state due to its reactivity. It occurs in combined state. It is most abundant halogen.

   It occurs at an extent 0.14% in Earth crust. Some minerals containing chlorine is

   (i) Rock salt : NaCl

   (ii) Carnalite : $KCl.MgCl_2, 6H_2O$

   (iii) Sylvine : KCl

   (iv) Horn silver : AgCl

   The other important commercial source of chlorine are KCl, MgCl and $CaCl_2$. Sea water contains about 28% in form of chlorides.

2. **Preparation of chlorides [General Method] :**

   (i) By the oxidation of hydrochloric acid.

   (a) From Manganese dioxide : MnO_2 oxidizes HCl to Cl_2 as per the following reactions.

   $$MnO_2 + 4HCl \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$$

   (b) Lead dioxide or red lead : Chlorine can be obtained by treating lead dioxide or red lead with HCl

   $$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$$

   $$\underset{\text{Red lead}}{Pb_3O_4} + 8HCl \longrightarrow 3PbCl_2 + Cl_2 + 4H_2O$$

   (c) Potassium permaganate by the action of concentrated HCl

   $$2KMnO_4 + 6HCl + 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

   (d) Potassium dichromate by the action of HCl

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

(ii) By the action of mineral acid on bleaching powder. Chlorine can also be obtained by treating bleaching powder ($CaOCl_2$) with minerals acid. Such as dil HCl or dil. H_2SO_4.

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + Cl_2 + H_2O$$

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + Cl_2 + H_2O$$

(iii) By the action of Conc. H_2SO_4 on NaCl in presence of MnO_2.

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + Cl_2 + 2H_2O$$

MANUFACTURE OF CHLORINE :

(i) **Deacon process :** Hydrogen chlrine gas is oxidized by atomospheric oxygen is presence of $CuCl_2$ (catalyst) at 723 K.

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

(ii) **Electrolytic process :** The process is used for the Manufacture of sodium hydroxide when chlorine is obtained as a by product. During electrolysis of brine hydrogen gas liberates at cathode, whereas chlorine gas liberate at anode. Since chlorine react with NaOH and H_2 the cathode must be separated from anode chlorine evolved and does not come is contact with NaOH or H_2 produced at cathode.

3. Properties of chlorine :

(i) **Physical properties :** It is greenish yellow gas with a characteristic pugent and suffocating odour.

(ii) It is heavier than air

(iii) It is poisonous gas when inhaled it cause headache and irritation of nose throat and lungs. It may proved fatal is inhaled in large quantities.

(iv) It can be liquified easily into greenish yellow liquid which boils at 293K.

(v) It is solube in water and called as chlorine water. It smells of Cl_2 on cooling the aqueous solution of chlorine gas yellow crystal of Cl_28H_2O.

Chemical properties :

(i) **Combustibility :** Chlorine is neither combustible nor a supporter of combustion.

(ii) **Combination with metals :** It react with a number of metals to from their chlorides. The action of chlorine on metal increase with increase in the activity of metal.

eg : Sodium and other alkali metals, Ca etc. burn spontaneously in chlorine and form their respective chlorides.

(i) $2Na + Cl_2 \longrightarrow 2NaCl$

(ii) $2K + Cl_2 \longrightarrow 2KCl$

(iii) $Ca + Cl_2 \longrightarrow CaCl_2$

It combines with iron and aluminium when they are heated in a current of chlorine.

(i) $2Fe + 3Cl_2 \xrightarrow{\Delta} 2FeCl_3$

(ii) $2Al + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3$

This chlorine leaves on being thrown in ajar of chlorine each fire and form cupric acid.

$Cu + Cl_2 \xrightarrow{\Delta} CuCl_2$

(iii) Reaction with waters : In absence of sunlight chlroine dissolves in water at ordinary temperature to form mixture of HCl and HOCl.

$$Cl_2 + H_2O \rightleftharpoons HCl + \underset{\text{Hypochlorous acid}}{HOCl}$$

HOCl is not much stable and decomposes on standing on exposive to sunlight to give HOCl and O_2.

$2HOCl \longrightarrow 2HCl + O_2$

Hence chlorine is a powerful bleaching and oxidizing agent.

(iv) Combination with non-metals : It combines directly with several metalloids and non-metals such as arsenic, antimony, sulphur, phosphorus, boron to form respective chlorides.

(i) $2As + 3Cl_2 \longrightarrow 2AsCl_3$

(ii) $2Sb + 3Cl_2 \longrightarrow 2SbCl_3$

(iii) $2S + Cl_2 \longrightarrow \underset{\text{Sulphur mono chloride}}{S_2Cl_2}$

(iv) $P_4 + 6Cl_2 \longrightarrow 4PbCl_3$

(v) $P_4 + 10Cl_2 \longrightarrow 4PCl_5$

(vi) $2B + 3Cl_2 \longrightarrow 2BCl_3$

(v) Affinity for hydrogen - chlorine has very high affinity for hydrogen. It combines with hydrogen in presence of diffused sunlight to form hydrogen chloride.

$H_2 + Cl_2 \longrightarrow 2HCl$

It has so much affinity for hydrogen that it can remove hydrogen from hydrocarbons. A burning candle on a paper soaked in terpentine oil continues burning in it with decomposition of hydrocarbons.

$$\underset{\text{Terpentine oil}}{C_{10}H_6} + 8Cl_2 \longrightarrow 16HCl + 10C$$

(vi) Reaction with ammonia : Chlorine react with excess of ammonia to form ammonium chloride and nitrogen.

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

However if chlorine is in excess nitrogen tri-chloride is obtained in place of nitrogen which is explosive.

$$\underset{\text{(Excess)}}{3Cl_2} + NH_3 \longrightarrow 3HCl + \underset{\text{Nitrogen tri-chloride}}{NCl_3}$$

(vii) Reaction with CS_2 : If forms CCl_4

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

$$2S_2Cl_2 + CS_2 \longrightarrow CCl_4 + 6S$$

(viii) Bleaching action : Due to its oxidizing nature, chlorine acts as a powerful bleaching agent.

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

vegetable colouring matter $+(O) \longrightarrow$ colourless matter.

(ix) Disinfecting actions : Due to its ability of killing harmful micro-organism. This ability is again due to its oxidizing nature.

(x) Oxidizing nature of chlorine

(i) It oxidizes ferrous salt to ferric salts

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

(ii) It oxidize sulphites to a sulphates

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

(iii) Its oxidizes H_2S to sulphur.

$$Cl_2 + H_2S \longrightarrow S + 2HCl$$

(iv) It oxidizen SO_2 to H_2SO_4

$$Cl_2 + SO_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4$$

(xi) Reaction with alkalies : When chlorine is passed through cold and dilute caustic soda solution of a mixture of hypochlorite and chloride is formed

$$\underset{\text{(Cold and Dilute)}}{Cl_2 + 2NaOH} \longrightarrow NaCl + NaOCl + H_2O$$

$$2Cl_2 + 2Ca(OH)_2 \xrightarrow{\text{Cold}} CaCl_2 + \underset{\text{Calcium hypochlorite}}{Ca(OCl)_2} + 2H_2O$$

With hot and concentrated solution of caustic soda. Chlorine react to produce chlorate and chloride.

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

When chloride is passed owed dry slaked lime, bleaching powder is obtained.

$$Ca(OH)_2 + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{CaOCl_2} + H_2O$$

(xii) Displacement of bromine and Iodine

$$2KBr_{(aq)} + Cl_2 \longrightarrow 2KCl + Br_2$$

$$2KI_{(aq)} + Cl_2 \longrightarrow 2KCl + I_2$$

(xiii) Reaction with hydrocarbons - with saturated hydrocarbons, chlorine forms substitution products.

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

With unsaturated hydrocarbons it gives addition products.

$$CH_2 = CH_2 + Cl_2 \xrightarrow[\text{temp.}]{\text{room}} CH_2Cl - CH_2Cl$$

(xiv) Formation of addition products : In the presence of sunlight chlorine combine with several compounds such as SO_2, CO to form addition products.

(i) $SO + Cl_2 \xrightarrow{\text{sun light}} \underset{\text{Sulphuryl chloride}}{SO_2Cl_2}$

(ii) $\underset{\text{Carbonyl chloride (phosgene)}}{CO + Cl_2 \xrightarrow{\text{Sun light}} COCl_2}$

4. Uses of chlorides :

(i) As bleaching agent in textile and paper industry.

(ii) For the sterilization of Muncipal supply of water.

(iii) In the extraction of metals like gold and platinum.

(iv) In the manufacture of bleaching powder.

(v) In the manufacture of dyestuff and explosive.

(vi) In the manufacture of refrigerant such as freon (i.e. CCl_2F_2)

(vii) In the manufacture of several poisonous gases such as mustard gas, phosgene etc.

Which is used in nearfare. It is also used in the manufacture of tear gas.

(viii) In manufacture of hypochlorite, chlorates, Perchearates, hydrochloric acid etc.

(ix) In the manufacture of several industry important solvent such as chloroform CCl_4 and ethylene chloride etc.

(x) In the manufacture of synthetic plastic such as PVC.

(xi) In the manufacture of insecticides like DDT, BHC etc.