CHAPTER

36

Oxides, Oxyacids, Halides and Oxyhalides of Sulphur

Oxides

I. Sulphur Dioxide, SO_2.

It may be prepared by the reactions given below :

$$S + O_2 \longrightarrow SO_2$$

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

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

It is a colourless gas having a pungent suffocating odour. It is highly soluble in H_2O and the solution so obtained is called *susphurous acid.* Thus SO_2 is an acidic oxide and is called *sulphurous acid anhydride.* Aqueous solution of SO_2 is a strong reducing agent.

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

Thus this gas reduces halogens to their respective halogen acids, $Fe_2(SO_4)_3$ to $FeSO_4$, iodates to I_2 etc. SO_2 also acts as an oxidising agent and hence oxidises H_2S to S, Fe to FeO, Mg to MgO, H_2 to H_2O, CO to CO_2, $SnCl_2$ to $SnCl_4$, Hg_2Cl_2 to $HgCl_2$ etc. In the presence of moisture, SO_2 bleaches vegetable colouring matter and hence is used as a bleaching agent. SO_2 is used : (*i*) for bleaching delicate articles like wool, straw silk and hair which are likely to be damaged by chlorine. (*ii*) for household fumigation. (*iii*) in the manufacture of sulphuric acid and sulphites, (*iv*) for the refining and bleaching for sugar, (*v*) in the liquid form for purifying petroleum and as a solvent for iodine, sulphur and phosphorus, and (*vi*) as a refrigerant. Cooling is caused when liquid sulphur dioxide is allowed to evaporate.

SO_2 molecule is a covalent molecule. In the gaseous as well as in the solid state it exists as a discrete molecule. The structure of this molecule is $O=\overset{\times\times}{S}=O$ and it has *angular shape* which results from sp^2 hybridisation of S-atom (central atom). The structure and shape of SO_2 molecule on the basis of sp^2 hybridisation of S-atom has already been explained.

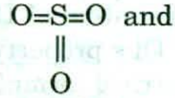
II. Sulphur Trioxide SO_3.

This oxide is prepared by the reactions shown below :

$$2SO_2 + O_2 \xrightarrow[450°C]{\text{Platinised asbestos}} 2SO_3$$

$$Fe_2(SO_4)_3 \xrightarrow[1150]{\Delta} Fe_2O_3 + 3SO_3$$

At room temperature it is liquid which strongly fumes in air. SO_3 exists in three varieties which are α-SO_3, β-SO_3, and γ-SO_3. It combines with H_2O with a hissing sound, forming H_2SO_4. It oxidizes S to SO_2, P to P_2O_5 and KI to I_2. SO_3 is used as a solvent, for the manufacture of sulphuric acid and as a drying agent for gases.

SO_3 molecule is a covalent molecule. In the gaseous state it exists as a discrete molecule. The structure of this molecule is  $O=\underset{\underset{O}{\|}}{S}=O$ and it has *trigonal planar geometry* which results from sp^2 hybridisation of S-atom (central atom). The structure and shape of SO_3 molecule on the basis of sp^2 hybridisation of S-atom has already been explained.

Oxy Acids

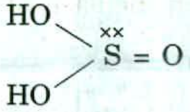
Sulphur forms a large number of oxy-acids. To emphasize their structural similarities, these acids have been classified into five groups (1) *Sulphoxylic acid, H_2SO_2* which is not known in the free state (2) *Sulphurous acids.* Examples are sulphurous acid, H_2SO_3 (not known in the free state); hyposulphurous acid or hydrosulphurous acid or dithionous acid, $H_2S_2O_4$ (not known in the free state); thiosulphurous acid, $H_2S_2O_2$; disulphurous or pyrosulphurous acid, $H_2S_2O_5$ (not known in the free state) (3) *Sulphuric acids.* Examples are sulphuric acid, H_2SO_4; thiosulphuric acid, $H_2S_2O_3$; pyrosulphuric acid or disulphuric acid, $H_2S_2O_7$ (4) *Thionic acids.* Examples are dithionic acid, $H_2S_2O_6$; polythionic acids. $H_2S_nO_6$ (n = 3, 4, 5, 6) (5) *Peroxy (or peroxo or per) sulphuric acids.* Examples are peroxomonosulphuric acid or permono sulphuric acid (also called Caro's acid), H_2SO_5 and peroxodisulpuric acid or perdisuiphuric acid (also called Marshall's acid), $H_2S_2O_8$. Here we shall discuss only a few acids.

I. Sulphurous Acid, H_2SO_3.

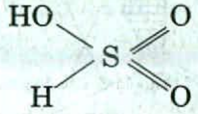
This acid is known only in solution and is formed by dissolving SO_2 in H_2O. This acid acts as an oxiding agent towards strong reducing agents. Thus H_2S is oxidised to S, HI to I_2 etc. It is a dibasic acid and ionises as :

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^- \; ; \; HSO_3^- \rightleftarrows H^+ + SO_3^{2-}$$

Following two structures have been suggested for the acid. One of these structures is symmetrical and has tetrahedral shape while the other is unsymmetrical and has pyramidal shape.



Symmetrical structure
(Tetrahedral shape)

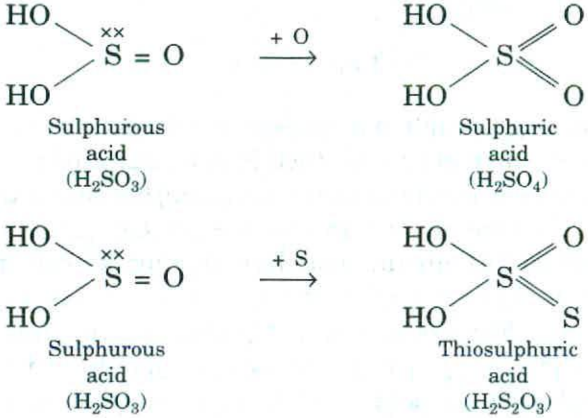


Unsymmetrical structure
(Pyramidal shape)

The following points are in favour of symmetrical structure of the acid :

(*i*) The preparation of sulphurous acid by the action of water on thionyl chloride suggests the symmetrical formula.

(*ii*) H_2SO_3 readily takes up one oxygen or sulphur atom which gets attached with the sulphur atom of H_2SO_3 to give sulphuric acid (H_2SO_4) or thiosulphuric acid ($H_2S_2O_5$). This property of H_2SO_3 can be explained if we assume that H_2SO_3 has the symmetrical formula shown above. The lone pair of electrons on sulphur atom in H_2SO_3 can easily be shared by another oxygen or sulphur atom to produce H_2SO_4 or $H_2S_2O_3$.



The unsymmetrical structure which contains S—H bond explains the reducing property of H_2SO_3. Now it is believed that the two forms of the acid shown above exist in equilibrium with each other. X-ray analysis of the ionic crystals containing SO_3^{2-} ion has shown that SO_3^{2-} ion has *pyramidal shape* (Fig. 36.1). This shape has three O-atoms in a triangle and results form sp^3 hybridisation of S-atom (central atom). In this structure all the S—O bond lengths are 1.39 A°. S—O π bond is d(S)—p(O) π bond.

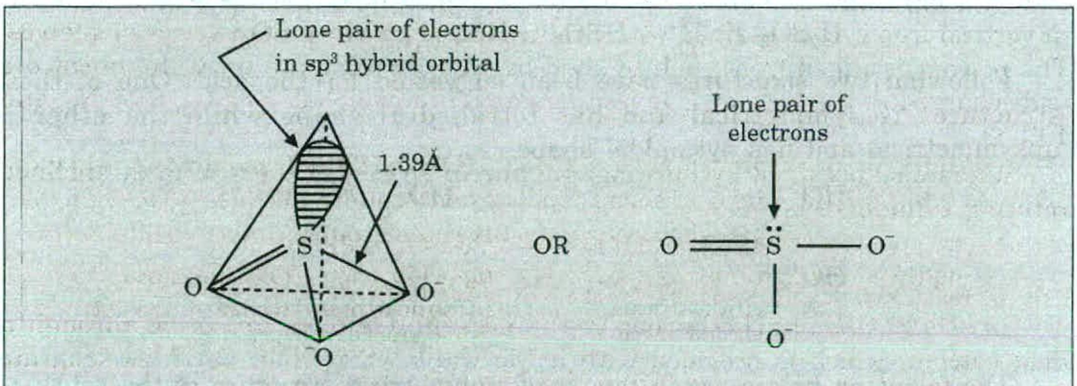


Fig. 36.1. Pyramidal shape of $SO^{2-}{}_3$ ion.

III. Sulphuric Acid, H_2SO_4.

This acid is manufactured by the following processes.

1. Lead Chamber Process. In this process sulphuric acid is obtained by the oxidation of SO_2 by nitrogen dioxide, NO_2. The simplest explanation of the changes taking place is due to Berzelius. According to him sulphur dioxide is first oxidised by nitrogen dioxide to sulphur trioxide which reacts with steam forming sulphuric acid. Nitrogen dioxide itself is reduced to nitric oxide, NO which is subsequently oxidised back to nitrogen dioxide by atmospheric oxygen. The various reactions are represented as follows :

$$\begin{aligned} SO_2 + NO_2 &\longrightarrow SO_3 + NO \\ SO_3 + H_2O\ (\textit{Steam}) &\longrightarrow H_2SO_4 \\ 2NO + O_2\ (\textit{From air}) &\longrightarrow 2NO_2 \end{aligned}$$

Thus NO and NO_2 act as oxygen carriers. *i.e.* they transfer oxygen from the air to sulphur dioxide.

It is, however, observed that if the chambers are *insufficiently supplied with steam, lead chamber crystals are formed* which consist of nitroso-sulphuric acid, $HSO_4.NO$. The simple theory given by Berzelius as outlined above does not explain the formation of $HSO_4.NO$. Hence it has been suggested by Davy and Lunge that the nitroso acid is formed as an intermediate product during the formation of sulphuric acid as follows :

$$\begin{aligned} NO + NO_2 &\longrightarrow N_2O_3 \\ 2SO_2 + N_2O_3 + O_2 + H_2O &\longrightarrow 2HSO_4.NO \\ 2HSO_4.NO + H_2O &\longrightarrow 2H_2SO_4 + NO + NO_2 \end{aligned}$$

Here it must be noted that the fact that nitroso-sulphuric acid is formed if insufficient steam is present, does not prove that it is formed as an intermediate product under normal working conditions.

Plant Used and Procedure. The various parts of the plant along with their functions are described below. The plant is shown diagrammatically in Fig. 36.2.

(*i*) *Pyrites burners or sulphur burners.* These are brick furnaces in which sulphur or iron pyrites in lumps is burnt, the supply of air being regulated by sliding doors below and above the pyrites. Spent oxide or pyrites powder is burnt in vertical iron cylinders lined with firebricks and provided with series of shelves. The powder is raked from shelf to shelf by rotating scrapers until the burnt ore is discharged at the bottom. The issuing gas contains about 7% SO_2, 83% N_2, and 10% O_2.

SO_2 is also obtained by burning sulphur in special burners of large inclined rotating cylinders.

$$\begin{aligned} 4FeS_2 + 11O_2 &\longrightarrow 2Fe_2O_3 + 8SO_2 \\ S + O_2 &\longrightarrow SO_2 \end{aligned}$$

(*ii*) *Dust catcher.* The burner gas is passed, if pyrites are used, through a dust catcher, which is provided with baffle walls where dust particles separate due to gravity. This may also be done by passing through Cottrell electrostatic dust precipitator.

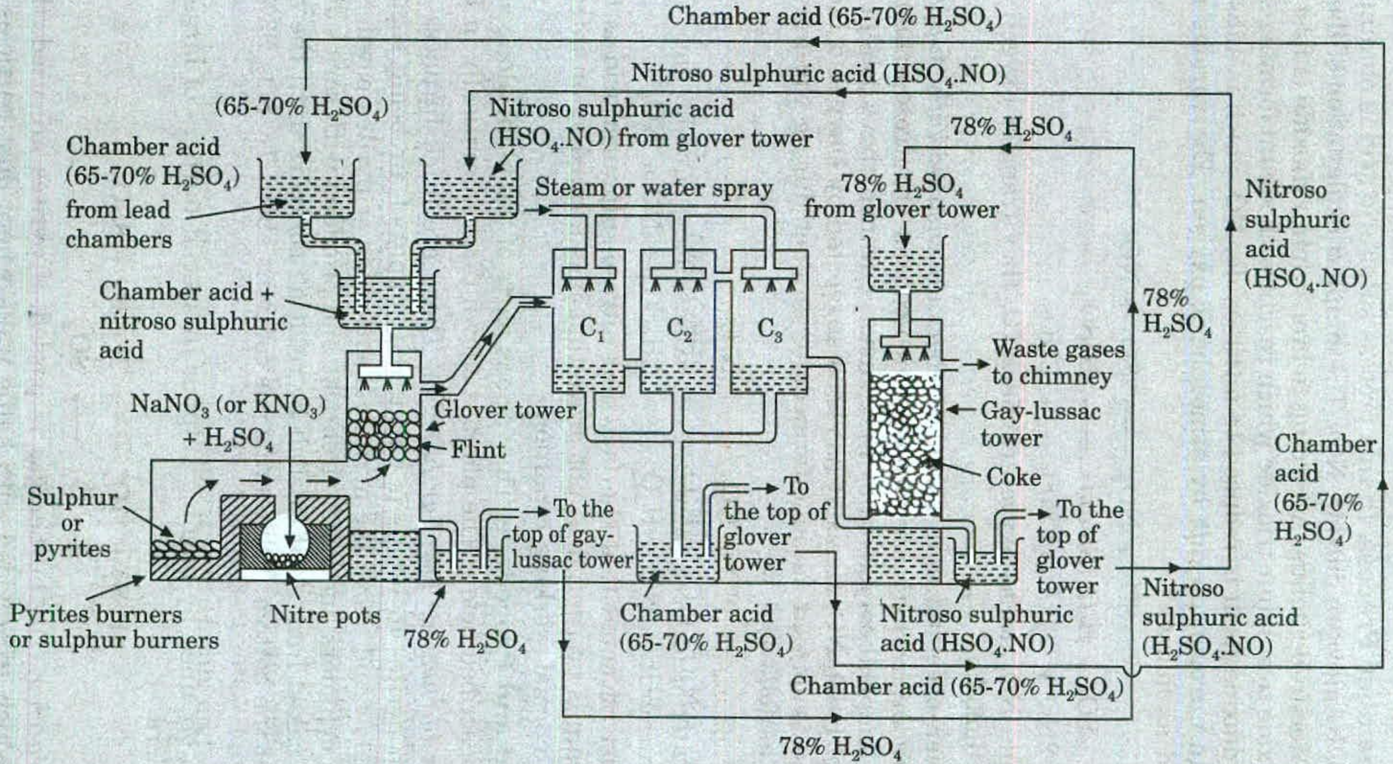


Fig. 36.2 Parts of the plant used for the manufacture of sulphuric acid by lead chamber process.

(*iii*) *Nitre pots.* Here $NaNO_3$ or KNO_3 is heated with conc. H_2SO_4 to produce nitric acid vapour.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

This nitric acid vapour mixes with the hot gases coming from the sulphur burners and going to glover tower and is reduced by SO_2 to give a mixture of NO and NO_2

$$2HNO_3 + SO_2 \longrightarrow H_2SO_4 + 2NO_2$$

In modern plants, the oxides of nitrogen are produced by the catalytic oxidation of NH_3.

$$4NH_3 + 5O_2 \xrightarrow[750\text{–}900^\circ C]{\text{Pt guaze}} 4NO + 6H_2O + 216 \text{ K.cals.}$$

$$2NO + O_2 \longrightarrow 2NO_2$$

(*iv*) *Glover tower* (or *Denitrating tower*). The gases now enter the glower tower near the base. The tower is of lead, lined inside with acid resisting material and packed with flint. There are two tanks at the top. One contains the dilute chamber acid and the second the nitrated acid (*i.e.* nitroso-sulphuric acid, $NO.HSO_4$) from the base of Gay-Lussac tower. Both these acids flow down slowly over flint pieces and meet an ascending stream of hot gases. There are four functions of this tower :

(*a*) The burner gases at 330—440°C are cooled to 50–80°C.

(*b*) The nitrated acid loses the dissolved oxides of nitrogen because these are taken by the burner gases.

$$2NO.HSO_4 + H_2O \longrightarrow 2H_2SO_4 + NO + NO_2$$

(*c*) The chamber acid is concentrated to about 80%.

(*d*) Sulphur dioxide is partly oxidised to sulphuric acid.

Sulphuric acid is always drawn from the bottom of the glover tower and is about 80%.

(*v*) *Lead chambers.* The gases (SO_2, O_2, oxides of nitrogen and moisture) are then led to a set of three or more large lead chambers (shown as C_1, C_2 and C_3 in Figure 36.2) which are made of lead and supported in wooden frames. The capacity of each lead chamber is 2503–7503 cu. feet and they are connected by means of wide lead pipes. Steam from a low-pressure boiler or more usually a very fine spray of water is admitted into these chambers from the top as shown in the figure when dil. H_2SO_4 is formed by the interaction of SO_2, oxides of nitrogen and H_2O.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
$$H_2SO_3 + NO_2 \longrightarrow H_2SO_4 + NO$$
$$2NO + O_2 \longrightarrow 2NO_2$$

Dilute H_2SO_4 so formed flows down in a common receiver placed at the floor of the chambers. It is called *chamber acid* and contains 65–70% H_2SO_4. It is pumped to the glover tower for its further concentration. In these chambers about 98% of SO_2 is converted into H_2SO_4.

(*vi*) *Gay-Lussac tower.* The residual gases coming from the last lead chamber contain N_2, a little O_2, oxides of nitrogen and traces of SO_2 and are led to the Gay-Lussac tower. This tower is lined with lead, and is 40 to 60 feet high and 8 to 15 feet in diameter. It is packed with coke down which flows a stream of cold 78% H_2SO_4 coming from the base of glover tower. This acid absorbs oxides of nitrogen in the exit gases of the lead chambers forming nitroso.sulphuric acid, $HSO_4.NO$.

$$2H_2SO_4 + NO + NO_2 \longrightarrow 2HSO_4.NO + H_2O$$

The nitroso-sulphuric acid so produced collects at the base of Gay-Lussac tower and is pumped to the top of the glover tower for the recovery of the oxides.

(*vii*) *Chimney.* The waste gas from the Gay-Lussac tower is left off into the atmosphere by passing through a chimney which is placed on the extreme right of the plant (not shown in the figure), thus creating a draught (partial vacuum) which helps in drawing the gases through the plant.

Impurities Present in the Chamber Acid and Their Removal. The chief impurities present in the chamber acid are arsenious oxide, lead sulphate and oxides of nitrogen. These are removed as follows :

(*i*) *Lead sulphate* comes in as an impurity sometimes by the action of acid on the lead of the chambers. It is removed by diluting the acid when the insoluble lead sulphate is separated.

(*ii*) *Arsenious oxide* (from the pyrites) is removed by passing sulphuretted hydrogen through the dilute acid, when it is precipitated in the form of sulphide.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

It is removed by filtration under reduced pressure through unglazed earthenware plates or by flotation with paraffin which comes to the surface gathering all the precipitate with it.

(*iii*) *The oxides of nitrogen* are expelled by distilling the diluted acid with ammomum sulphate. The oxides of nitrogen are reduced to elementary nitrogen which escapes.

$$(NH_4)_2SO_4 + NO + NO_2 \longrightarrow 2N_2 + H_2SO_4 + 3H_2O$$

It is not always necessary to purify the chamber acid. For most purposes it is used as such. Whenever pure acid is needed it is prepared by the *contact process* rather than by the purification of chamber acid.

Concentration of the Chamber Acid. The acid obtained from glover tower contains about 78% H_2SO_4. Acid of this strength is known as *Brown Oil of Vitriol* (*B.O.V.*) on account of its colour which is due to the presence of impurities in it. It is further concentrated to form the acid containing 93–95% H_2SO_4. This concentrated acid is called *Rectified Oil of Vitriol* (*R.O.V.*)

The chamber acid is concentrated by : (*i*) *Cascade process* and (*ii*) *Gaillard process.* The principle involved in both the processes is to evaporate water present in the acid by bringing the dilute acid in contact with hot gases. The difference lies in the exposure of the dilute acid to the hot gases. The dilute acid and the hot gases come in contact with each other on the counter-current principle.

(*i*) *Cascade process.* (Fig. 36.3). The concentration of the acid is done in this process by heating the acid in fused silica basins arranged in such a way that the acid passes from the upper basin to the lower one as it goes on being concentrated. The heating is done by means of hot gases playing below the basins and as the acid passes downwards it is subjected to stronger heat, so that by the time it reaches the lowermost basin it has been concentrated to the maximum. The acid vapour along with the steam is taken to a recovery *plant* while the *concentrated* acid is taken to storage tanks.

(*ii*) *Gaillard process.* (Fig. 36.4). The acid is introduced in the form of a fine spray from the top of a tower (called *Gaillard tower*) built of acid-resisting stone, up which hot gases are passed. During the passage downwards the droplets of the dilute acid come in contact with the hot gases and lose their water so that by the time the acid reaches the bottom, it has been concentrated to about 95% pure acid.

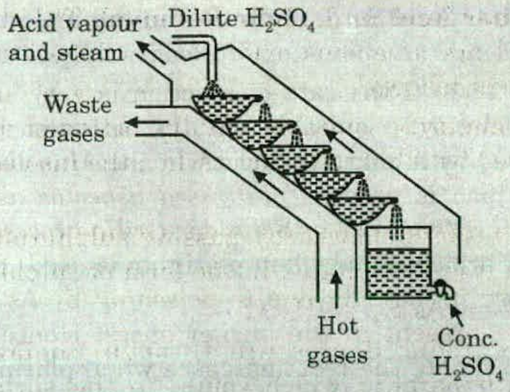


Fig. 36.3. Concentration of H_2SO_4 by Cascade process.

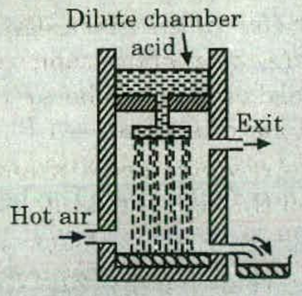


Fig. 36.4. Concentration of H_2SO_4 by Gaillard process.

The last traces of water are removed by adding sulphur trioxide to the acid which combines with the excess of water to form sulphuric acid.

2. Contact Process. Sulphur dioxide obtained by the burning of sulphur or pyrites (FeS_2) is made to combine with oxygen under suitable conditions in order to get sulphur trioxide.

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + 45{,}000 \text{ cals.}$$

The sulphur trioxide so formed is dissolved in sulphuric acid and the *oleum* or *pyrosulphuric acid* ($H_2S_2O_7$) which results is diluted with water to get sulphuric acid of required concentration.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Conditions for Maximum Yield of SO_3. We have seen that in this process we make use of the reaction,

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + 45{,}000 \text{ cals.}$$

which is *reversible, exothermic* and proceeds with a *decrease* in *volume* (*i.e.* 3 volumes change to 2 volumes). According to Le-Chatelier's principle the formation of SO_3 is favoured by :

(i) Low temperature. This reaction is exothermic, naturally the formation of SO_2 does not require high temperature. At low temperatures no reaction takes place between SO_2 and O_2. Thus a temperature between 400°—600°C is maintained and the reaction occurs with adequate speed.

(ii) High pressure. Since the reaction proceeds in the forward direction with decrease in volume, *i.e.* 3 volumes change to 2 volumes, a high pressure will favour the formation of SO_3. The gases are given a pressure of two atmospheres. High pressures may bring about greater corrosion of the chambers.

(iii) Excess of oxygen. A slight excess of oxygen in the reacting mixture of $SO_2 + O_2$ helps to carry the reaction in the direction of the formation of sulphur trioxide. Best results are obtained when O_2 and SO_2 are present in the molecular proportion of 3 : 2.

(iv) Use of catalyst. Even at 400°–500°C the rate of reaction is very slow. Therefore, to increase the reaction velocity, a suitable catalyst is used. The commonly used catalysts are : (*a*) Fe_2O_3 with a little CuO as in the *Mannheim process.* (*b*) V_2O_5, and (*c*) Platinum which is used as *platinised asbestos as in Badische proress, platinised magnesium sulphate as in Schroder-Grillo process or as platinised silica gel.* The best results are obtained when platinum is used. But, platinum is very costly and rapidly lose its activity due to *poisoning* by As_2O_3, sulphuric acid fog, dust etc. which are present in the burner gases. Hence an utmost care has to be taken for purification of the reacting gases when platinum is used as a catalyst. Platinised silica gel is, however, immune to arsenic poisoning. Now-a-days most of the sulphuric acid plants use V_2O_5 as a catalyst in place of platinum because it is cheaper and is not easily poisoned, How ever, it cannot be recovered after use.

Plant Used and Procedure. The plant used is shown diagrammatically in Fig. 36.5. It consists of four essential parts :

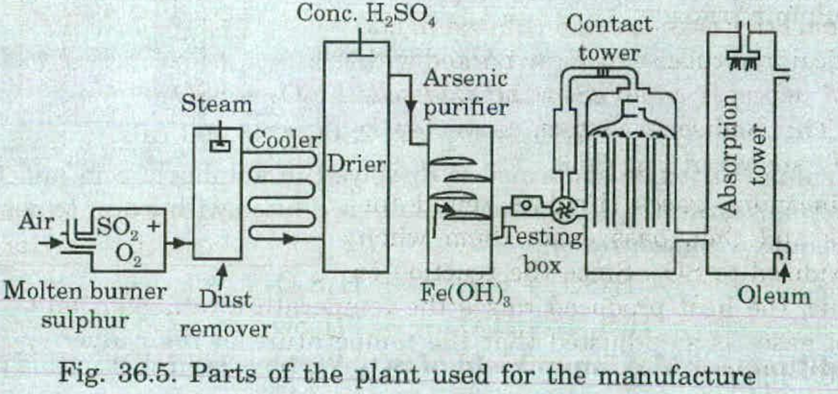


Fig. 36.5. Parts of the plant used for the manufacture of sulphuric acid by contact process.

(i) Sulphur burners. In these sulphur or pyrites (FeS_2) is burnt to get sulphur dioxide.

$$S + O_2 \longrightarrow SO_2$$
$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$
$$2S + 3O_2 \longrightarrow 2SO_3$$

Traces of SO_3 are also produced which give sulphuric acid fog with water vapours present in air.

(ii) Purification unit. The gases from sulphur burners containing about 8% SO_2, 1% O_2 and the rest N_2 are not pure. They contain impurities of As_2O_3, sulphur dust and sulphuric acid fog which act as poisons on the catalytic surface. Hence they are *purified* thoroughly by passing in succession through : (*a*) *a dust remover* in which the heavy dust particles are removed by mechanical precipitation aided by steam or electrically by using the *Cottrell process.* (*b*) *a series of cooling pipes* (*i.e., cooler*) to reduce the temperature to about 100°C. (*c*) *a scrubber* (*washing tower—not shown in Fig. 36.5*) where the gases meet a descending spray of water which removes the *acid fog.* Most of the dust which could not be removed in the dust remover gets washed off here with a spray of water. The gases, however, *moist.* (*d*) *a drying tower* (*drier*) which is packed with coke or flint stone and down which a stream of cone. H_2SO_4 flows. Here the gases are dried. (*e*) *an arsenic purifier* which contains precipitated $Fe(OH)_3$ placed on horizontal shelves. $Fe(OH)_3$ absorbs As_2O_3, if present as impurity in the gases. (*f*) *a testing box* in which a strong beam of light is thrown against the gases in order to be sure that the gases are absolutely free from dust and As_2O_3 particles. If any particles are present, they are illuminated due to the Tyndall effect.

(iii) Preheater and contact converter (or tower). The purified gases are then led into the *preheater* (P) where the gases are preheated to 400°–450°C (*optimum temperature*) by the hot gases (mainly SO_3 and N_2) from the converter which are themselves thereby cooled. The hot gases now enter into an iron cylinder which is called a *contact converter* or *tower* and is fitted inside with vertical iron tubes which are packed with platinised asbestos catalyst in the *Badische process.* The Badische contact converter is separately shown in Fig. 36.6.

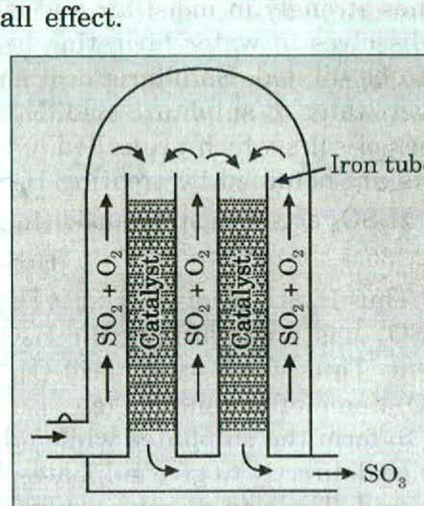


Fig. 36.6. Badische contact converter

The incoming gases circulate round the hot tubes and then pass down them when SO_2 is oxidised to SO_3. Since the reaction is exothermic, the heat produced raises the temperature to about 580°C. The rate of flow of gases is so adjusted that the temperature in the converter is kept to about 400°–450°C.

***(iv) Absorption tower*.** The sulphur trioxide formed in the converter is passed up an absorption tower where it meets a descending stream of concentrated sulphuric acid. The acid absorbs the sulphur trioxide to form *fuming sulphuric acid* or *oleum* which is then diluted with the calculated quantity of water to get sulphuric acid of the required concentration.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$
$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Water cannot be used for absorbing SO_3 because in doing so a large amount of heat is evolved resulting in the formation of a dense fog of minute particles of sulphuric acid which does not easily condense down.

Comparison Between the Contact Process and Chamber Process.

(*i*) Sulphuric acid obtained by the contact process is of higher purity than that obtained by the chamber process.

(*ii*) Sulphuric acid obtained by the contact process needs no further concentration. It is highly concentrated. The acid obtained by the chamber process is maximum 78% concentrated and needs further concentration.

(*iii*) The cost of production of sulphuric acid by chamber process is considered to be lower than that of the contact process because of the high cost of platinum metal but the use of vanadium pentoxide in place of platinum has reduced the cost of production in the contact process as well.

Properties of H_2SO_4.

Sulphuric acid is a colourless syrupy liquid of specific gravity 1.84 at 15°C. It fumes strongly in moist air and is highly corrosive. It is highly soluble in water. It dissolves in water liberating heat. Great care should be taken when the acid is to be diluted. Sulphuric acid should be added in a thin stream to water and never water to sulphuric acid. H_2SO_4 is strong dibasic acid and hence gives two types of salts which are called *bisulphates* (HSO_4^-) and *sulphates* (SO_4^{2-}). These salts are obtained by treating H_2SO_4 with alkalies.

H_2SO_4 acts as a strong oxidising agent, because it can supply an atom of oxygen.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + O$$

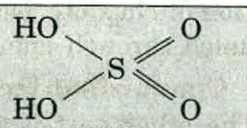
Thus H_2SO_4 oxidises S, C, P, HI and HBr to SO_2, H_3PO_3, I_2 and Br_2 respectively. H_2SO_4 has great affinity for H_2O and hence is used as a strong dehydrating agent. Thus when oxalic acid ($H_2C_2O_4$) is heated with H_2SO_4, the former loses H_2O. Some of the metals (*e.g.* Cu, Ag, Hg etc.) react with H_2SO_4 in presence of air to form the sulphates while other metals (*e.g.* Zn, Al, Zn, Mg etc.) react with the acid directly to give sulphates. Noble metals like Au and Pt. do not react with the acid. The acid dissolves sulphur trioxide forming fuming sulphuric acid, also called *oleum* or *pyrosulpluric acid*, $H_2S_2O_7$ which is much more active than sulphuric acid and forms the salts pyrosulphates which are extensively used in the manufacture of aniline dyes and explosives.

Uses of H_2SO_4.

H_2SO_4 is used (*i*) in the manufacture of chemical manures like *ammonium sulphate* and *calcium superphosphate.* (*ii*) in the manufacture of other acids like nitric acid, hydrochloric acid, phosphoric acid etc. (*iii*) in refining petroleum. (*iv*) in the manufacture of coal-tar dyes and a number of pharmaceuticals. (*v*) in the manufacture of explosives. (*vi*) in the textile, paper and dyeing industries. (*vii*) for cleansing metals before enamelling, electroplating, galvanising etc. (*pickling*). (*viii*) in storage batteries. (*ix*) in the manufacture of sulphates, bisulphates and sodium carbonate. (*x*) in the laboratory as an important reagent and as a drying and dehydrating agent.

Structure of H_2SO_4 Molecule and SO_4^{2-} Ion.

The structure of H_2SO_4 molecule is as shown in the margin.



Structure of H_2SO_4 molecule.

This structure is confirmed by the following facts :

(*i*) Sulphuric acid (H_2SO_4) contains two hydroxyl (OH) groups because it reacts with PCl_5 to give sulphuryl chloride (SO_2Cl_2) which in turn is hydrolysed by water to sulphuric acid. The structure of sulphuryl chloride is Cl_2SO_2 which is confirmed by the fact that SO_2Cl_2 can be obtained by the direct combination of SO_2 and Cl_2.

$$\underset{\text{Sulphuric acid}}{(HO)_2SO_2} + 2PCl_5 \longrightarrow \underset{\text{Sulphuryl chloride}}{Cl_2SO_2} + 2POCl_3 + 2HCl$$

$$Cl_2SO_2 + 2H.OH \longrightarrow (OH)_2SO_2 + 2HCl$$

$$SO_2 + Cl_2 \longrightarrow Cl_2SO_2$$

(*ii*) The two hydroxyl groups are symmetrically arranged in H_2SO_4 molecule because we get only one type of organic derivative like diethyl sulphone, $C_2H_5—SO_2—C_2H_5$. Both OH groups are directly linked to S-atom as is evident from the formation of diethyl sulphone, $(C_2H_5)_2SO_2$ by different routes :

$$(C_2H_5)_2S \xrightarrow{\text{Oxidation}} \underset{\text{Diethyl sulphone}}{(C_2H_5)_2SO_2} \xleftarrow{C_2H_6} Cl_2SO_2 \xleftarrow{PCl_5} H_2SO_4$$

(*iii*) When we consider the S—O bond lengths in H_2SO_4 molecule, we are suggested to believe that O-atoms are attached with S-atom by double bond.

X-ray analysis of the ionic crystals containing SO_4^{2-} ions has shown that SO_4^{2-} ion has *tetrahedral shape*. This shape results from sp^3 hydridisation of S-atom (central atom). Both S—O π bonds are $d(S)—p(O)$ π bonds.

III. Thioulphuric Acid, $H_2S_2O_3$.

The free acid is quite unstable at ordinary temperature but it has been isolated free from the solvent by reaction (*a*). It can also be obtained by treating $Na_2S_2O_3$ with very dil HCl as shown in reaction (*b*).

(*a*) $\underset{\text{Chlorosulphuric acid}}{OHSO_2Cl} + H_2S \longrightarrow H_2S_2O_3 + HCl;$

(*b*) $Na_2S_2O_3 + 2HCl \longrightarrow H_2S_2O_3 + 2NaCl$

The acid is very unstable and at once decomposes into SO_2 and S. The salts of $M_2S_2O_3$ type are called thiosulphates. Among thiosulphates, the most important is sodium thiosulphate (also called hypo), $Na_2S_2O_3$.

Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$.

It was formerly (wrongly) termed as *sodium hypo sulphate* or simply ***hypo*** and is still so called by photographers.

Preparation. (*i*) *By heating a solution of sodium sulphite with sulphur.* Sodium sulphite for this purpose may be obtained by passing sulphur dioxide through a solution of Na_2CO_3. The solution is divided into two equal parts. Sulphur dioxide is passed through one part till it is saturated with it.

$$Na_2CO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3 + CO_2$$

The other part is now added to convert the bisulphite into normal sodium sulphite.

$$2NaHSO_3 + Na_2CO_3 \longrightarrow 2Na_2SO_3 + H_2O + CO_2$$

This solution is boiled with sulphur until the alkaline reaction has disappeared.

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

The solution is filtered and the filtrate on concentration gives the crystals of sodium thiosulphate.

(*ii*) *By Spring reaction.* It is also prepared when requisite iodine is added to a mixture of sodium sulphite and sulphide solutions

$$Na_2S + Na_2SO_3 + I_2 \longrightarrow 2NaI + Na_2S_2O_3$$

In fact, any method which leads to the addition of sulphur to sodium sulphite would give thiosulphate.

(*iii*) It is obtained by the oxidation of soluble sulphides or hydrosulphides in air.

$$2NaHS + 2O_2 \longrightarrow Na_2S_2O_3 + H_2O$$

(*iv*) *Pure* sodium thiosulphate is formed by the interaction of sodium hydrosulphide (NaHS) and $NaHSO_3$ in solution and crystalling,

$$2NaHS + 4NaHSO_3 + I_2 \longrightarrow 2Na_2S_2O_3 + 3H_2O$$

Manufacture. It is manufactured from the waste liquor obtained in the manufacture of Na_2S. The waste liquor, still contains some Na_2S, Na_2CO_3, Na_2SO_3 and Na_2SO_4. The liquor is concentrated by evaporation and SO_2 is passed through it when $Na_2S_2O_3$ is formed.

$$Na_2SO_3 + 2Na_2S + 3SO_2 \longrightarrow 2Na_2S_2O_3$$

$$Na_2CO_3 + Na_2S + 4SO_2 \longrightarrow 3Na_2S_2O_3 + CO_2$$

The solution is filtered, concentrated and allowed to cool when colourless monoclinic crystals of $Na_2S_2O_2.5H_2O$ separate out.

Properties (*i*) *State*. It crystallises with five molecules of water of crystallisation. The crystals are colourless, dissolve in water and melt at 48°C. The water in combination is lost completely at 215°C.

(ii) Action of dilute acids. When treated with hydrochloric acid, thiosulphuric acid is temporarily formed but it decomposes almost immediately into sulphur dioxide and sulphur.

$$\begin{array}{rcl} Na_2S_2O_3 + 2HCl & \longrightarrow & 2NaCl + H_2S_2O_3 \\ H_2S_2O_3 & \longrightarrow & H_2O + SO_2 + S \\ \hline Na_2S_2O_3 + 2HCl & \longrightarrow & 2NaCl + H_2O + SO_2 + S \end{array}$$

(iii) Action of heat. On heating it melts at 48°C, loses its water of crystallisation at 215°C and decomposes above 223°C into Na_2SO_4 and sodium pentasulphide (Na_2S_5)

$$4Na_2S_2O_3 \xrightarrow[> 223^\circ]{\Delta} 3Na_2SO_4 + Na_2S_5$$

At higher temperature, Na_2S_5 loses some sulphur

$$Na_2S_5 \longrightarrow Na_2S_4 + S$$

(iv) Action of silver nitrate. With silver nitrate solution dilute solution of hypo forms an unstable white precipitate of $Ag_2S_2O_3$ which changes colour and eventually becomes black due to the formation of Ag_2S.

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow 2NaNO_3 + Ag_2S_2O_3$$

$$\underset{\text{White}}{Ag_2S_2O_3} + H_2O \longrightarrow \underset{\text{Black}}{Ag_2S} + H_2SO_4$$

Excess of $Na_2S_2O_3$, however, dissolves the precipitate of $Ag_2S_2O_3$ forming the complex sodium argento-thiosulphate, $Na[AgS_2O_3]$

$$Ag_2S_2O_3 + Na_2S_2O_3 \longrightarrow 2Na[AgS_2O_3]$$

(v) Action of silver halides. A solution of sodium thiosulphate dissolves silver halides (AgCl, AgBr, AgI) forming colourless complex—*sodium argento thiosulphate*, $Na_3[Ag(S_2O_3)_2]$. This property is utilized in the '*fixing*' of negatives and prints in photography as the thiosulphate solution removes the unaffected silver bromide.

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

(vi) Action of halogens. $Na_2S_2O_3$ is oxidised by chlorine or bromine water and sulphur is precipitated.

$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S$$

But with excess of halogens, S is oxidised to H_2SO_4

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaCl + 6HCl + 2H_2SO_4$$

It decolourises a solution of iodine giving a quantitative yield of *sodium tetrathionate*, $Na_2S_4O_6$

$$2Na_2S_2O_3 + I_2 \longrightarrow \underset{\substack{\text{Sod. tetra-}\\\text{thionate}}}{Na_2S_4O_6} + 3NaI$$

Hence this reaction is used in the volumetric estimation of iodine.

(vii) Action of $KMnO_4$. In *neutral* solution, $KMnO_4$ oxidises $Na_2S_2O_3$ to Na_2SO_4

$$Na_2S_2O_3 + 2KMnO_4 \longrightarrow Na_2SO_4 + K_2SO_4 + Mn_2O_3$$

In *acidic* solution, some sodium dithionate, $Na_2S_2O_6$ is also formed.

(viii) Action of ferric chloride solution. It gives a violet coloration with ferric chloride solution. The violet coloration is due to the formation of *ferric thiosulphate*, $Fe_2(S_2O_3)_3$.

$$3Na_2S_2O_3 + 2FeCl_3 \rightleftharpoons Fe_2(S_2O_3)_3 + 6NaCl$$

The colour rapidly disappears due to the reduction of ferric chloride to ferrous chloride.

$$\begin{array}{rcl} [FeCl_3 & \longrightarrow & FeCl_2 + Cl] \times 2 \\ 2Na_2S_2O_3 + 2Cl & \longrightarrow & Na_2S_4O_6 + 2NaCl \\ \hline 2Na_2S_2O_3 + 2FeCl_3 & \longrightarrow & 2NaCl + 2FeCl_2 + Na_2S_4O_6 \end{array}$$

(ix) Reaction with cupric salts. $Na_2S_2O_5$ first reduces cupric salts to cuprous salts which then dissolve in the excess of hypo forming a complex salt, *e.g.*

$$\begin{array}{rcl} \underset{(ic)}{2CuCl_2} + Na_2S_2O_3 & \longrightarrow & \underset{(ous)}{2CuCl} + Na_2S_4O_6 + 2NaCl \\ 2CuCl + Na_2S_2O_3 & \longrightarrow & Cu_2S_2O_3 + 2NaCl \\ 3Cu_2S_2O_3 + 2Na_2S_2O_3 & \longrightarrow & \underset{\text{Complex salt}}{Na_4[Cu_6(S_2O_3)_5]} \end{array}$$

(x) Reaction with auric salts. The action of $Na_2S_2O_3$ on auric salts is similar to that on cupric salts. Thus $Na_2S_2O_3$ first reduces auric salts to aurous salts which then dissolve in the excess of hypo forming a complex salt, *e.g.*

$$\begin{array}{rcl} \underset{(ic)}{AuCl_3} + 2Na_2S_2O_3 & \longrightarrow & \underset{(ous)}{AuCl} + Na_2S_4O_6 + 2NaCl \\ AuCl + 2Na_2S_2O_3 & \longrightarrow & \underset{\text{Sod. aurothio sulphate}}{Na_3[Au(S_2O_3)_2]} + NaCl \end{array}$$

(xi) Reaction with $HgCl_2$. $Na_2S_2O_3$ reacts with the excess of $HgCl_2$ liberating H_2SO_4 and forming a white precipitate of $HgCl_2.2HgS$

$$\begin{array}{rcl} [Na_2S_2O_3 + HgCl_2 & \longrightarrow & HgS_2O_3 + 2NaCl] \times 2 \\ [HgS_2O_3 + H_2O & \longrightarrow & HgS + H_2SO_4] \times 2 \\ HgCl_2 + 2HgS & \longrightarrow & HgCl_2.2HgS \\ \hline 2Na_2S_2O_3 + 3HgCl_2 + 2H_2O & \longrightarrow & 4NaCl + 2H_2SO_4 + \underset{\text{White ppt.}}{HgCl_2.2HgS} \end{array}$$

(xii) Reaction with bismuth salts. $Na_2S_2O_3$ with a solution of bismuth salt gives a clear solution of *sodium bismuth thiosulphate*, $Na_3[Bi(S_2O_3)_3]$

$$3Na_2S_2O_3 + Bi^{3+} \longrightarrow Na_3[Bi(S_2O_3)_3] + 3Na^+$$

The solution quickly decomposes and deposits black bismuth sulphide.

(xiii) Reaction with $BaCl_2$ and $CaCl_2$ solutions. A moderately concentrated solution of $Na_2S_2O_3$ gives a white precipitate of BaS_2O_3 with $BaCl_2$ solution.

$$Na_2S_2O_3 + BaCl_2 \longrightarrow \underset{\text{White ppt.}}{BaS_2O_3} + 2NaCl$$

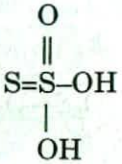
$CaCl_2$ gives no precipitate, since CaS_2O_3 is fairly soluble in H_2O

$$Na_2S_2O_3 + CaCl_2 \longrightarrow \underset{\text{Soluble}}{CaS_2O_3} + 2NaCl$$

Uses. It is used (*i*) *in photography.* Due to its property of dissolving Ag-halides, it is used as fixer in photography under the name s4ypo. It removes the excess of silver halides. (*ii*) *in textile industry.* During bleaching it is used as *antichlor* for removing excess of chlorine from bleaching fabrics. (*iii*) *in metallurgy.* It is used in the extraction of Au and Ag from their ores. (*iv*) *in the laboratory.* It is used for the estimation of iodine and as a reagent. (*v*) *in medicine.* It is also used in medicine.

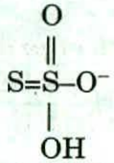
Structure of $H_2S_2O_3$ molecule and $S_2O_3^{2-}$ ion.

The structures of $H_2S_2O_3$ molecule and $S_2O_3^{2-}$ ion are as shown below :



$$S{=}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{S}}{-}OH$$

Structure of $H_2S_2O_3$ molecule



$$S{=}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{S}}{-}O^-$$

Structure of $S_2O_3^{2-}$ ion (Tetrahedral shape)

X-ray analysis of the ionic crystals containing $S_2O_3^{2-}$ ion has shown that $S_2O_3^{2-}$ has tetrahedral shape. This shape results from sp^3 hybridisation of S-atom (central atom).

The structure of $S_2O_3^{2-}$ ion as shown above indicates that the two S-atoms in $S_2O_3^{2-}$ ion are not equivalent in bonding and hence are not interchangeable. The presence of two different types of S-atoms in $S_2O_3^{2-}$ ion has been verified by the fact that a thiosulphate prepared from sulphite and radio-active sulphur (*e.g.* S^{35})

$$SO_3^{2-} + S^{35} \longrightarrow [S^{35} - SO_3]^{2-}$$

gets decomposed by acid to give exclusively radio active S^{35} and a non-radio active aqueous solution of SO_3^{2-} ions arising from SO_2 evolved.

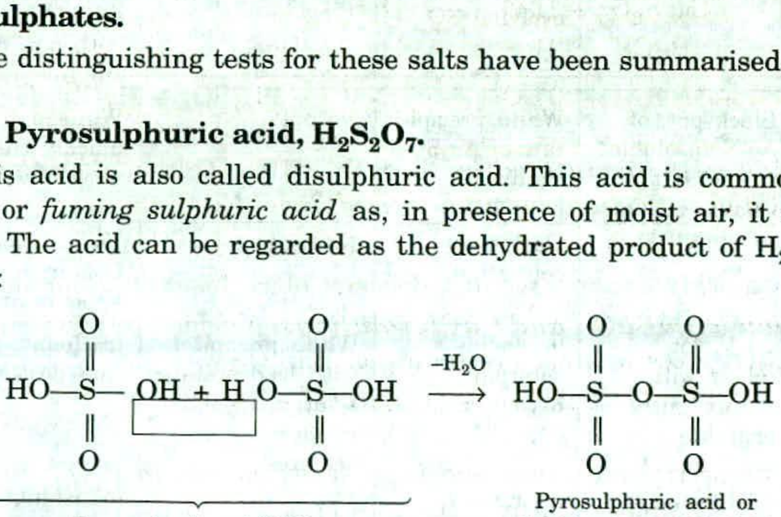
$$[S^{35} - SO_3]^{2-} + 2H^+ \longrightarrow S^{35} + H_2O + SO_2$$

Distinguishing Tests for Sulphides, Sulphites, Sulphates and Thiosulphates.

The distinguishing tests for these salts have been summarised in Table given 36.1.

IV. Pyrosulphuric acid, $H_2S_2O_7$.

This acid is also called disulphuric acid. This acid is commonly known as *oleum* or *fuming sulphuric acid* as, in presence of moist air, it releases white fumes. The acid can be regarded as the dehydrated product of H_2SO_4 as shown below :



$$\underbrace{HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\boxed{OH + H}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}_{\text{Two molecules of } H_2SO_4} \xrightarrow{-H_2O} HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$

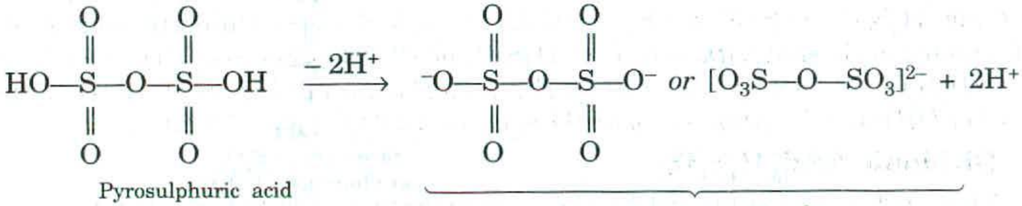
Two molecules of H_2SO_4

Pyrosulphuric acid or disulphuric acid ($H_2S_2O_7$)

This acid is isolated as a colourless crystaline solid (m. pt. = 36°C) by mixing equimolecular quantities of anhydrous H_2SO_4 and SO_3. The acid is very unstable and when dissolved in H_2O it gives H_2SO_4 molecule.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The fact that $H_2S_2O_7$ molecule can be regarded as being formed by the removal of one H_2O molecule from two H_2SO_4 molecules suggests that $H_2S_2O_7$ has the structure as shown below. X-ray diffraction studies of the ionic salts containing $S_2O_7^{2-}$ ion have shown that $S_2O_7^{2-}$ ion has $[O_3S{-}O{-}SO_3]^{2-}$ structure which has been shown at the right of that of $H_2S_2O_7$ molecule.



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH \xrightarrow{-2H^+} \underbrace{{}^-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^- \text{ or } [O_3S{-}O{-}SO_3]^{2-}}_{\text{Pyrosulphate ion } (S_2O_7^{2-})} + 2H^+$$

Pyrosulphuric acid ($H_2S_2O_7$)

Pyrosulphate ion ($S_2O_7^{2-}$)

Table 36.1. Comparison between sulphides, sulphites, sulphates and thiosulphates.

Test	Sulphide (S^{2-})	Sulphite (SO_3^{2-})	Sulphate (SO_4^{2-})	Thiosulphate ($S_2O_3^{2-}$)
1. *Action of dil. HCl*	H_2S is given off which turns lead acetate paper black.	SO_2 is given off which turns dichromate paper green.	No action	SO_2 and S are produced.
2. *Action of $BaCl_2$ solution*	No ppt.	Precipitate of $BaSO_3$ soluble in HNO_3 evolving SO_2.	White ppt. of $BaSO_4$ insoluble in HNO_3.	White ppt. of BaS_2O_3 from conc. solutions soluble in HNO_3 with ppt. of sulphur.
3. *Action of $AgNO_3$*	Black ppt. of Ag_2S insoluble in cold but soluble HNO_3.	White precipitate of Ag_2SO_3 soluble in HNO_3.	No ppt.	White ppt. but quickly changing to yelldw brown.
4. *Action of $FeCl_3$ solution*	Black ppt.	Dark red coloration.	No action	Violet coloration. Colour disappears at once.
5. *Confirmatory Test*	(*a*) Violet colour with sodium nitroprusside solution. (*b*) Black ppt. with lead acetate solution.	(*a*) Iodine solution decolorised. (*b*) $KMnO_4$ solution decolorised.	White precipitate with lead acetate solution insoluble in ammonium acetate.	(*a*) Iodine solution decolorised. (*b*) $KMnO_4$ solution decolorised.

Thionic Acids (H_2SnO_6)

The term thionic acids is used for the compounds in which two sulphonic groups, —SO_2OH *or* —SO_3H are linked together either directly or through one or more sulphur atoms. All the members of this class of acids can be represented by a general formula $H_2S_nO_6$ where $n = 2, 3, 4, 5, 6$. Thionic acids can be classified into two groups namely (*i*) *Dithionic acid*, $H_2S_2O_6$ ($n = 2$) in which two —SO_2OH groups are linked together directly. (*ii*) *Polythionic acids* in which two sulphonic groups, —SO_2OH or —SO_3H are linked together through one or more S-atoms. Thus all the members of polythionic acids can be represented by the general formula, $H_2S_nO_6$ or $HOO_2S—S_{n-2}—SO_2OH$ ($n = 3, 4, 5, 6$). Different members of polythionic acids are : *trithionic acid* ($H_2S_3O_6$ or $HOO_2S—S—SO_2OH$), *tetrathionic acid* ($H_2S_4O_6$ or $HOO_2S—S_2— SO_2OH$), *pentathionic acid* ($H_2S_5O_5$ *or* $HOO_2S—S_3—SO_2OH$) and *hexathionic acid* ($H_2S_6O_6$ *or* $HOO_2S—S_4—SO_2OH$).

Dithionic Acid, $H_2S_2O_6$.

This acid can be prepared by the slow oxidation of H_2SO_3 by MnO_2.

$$2H_2SO_3 + O \longrightarrow H_2S_2O_6 + H_2O$$

The aqueous solution of $H_2S_2O_6$ can be concentrated on a water bath and then in vacuum over H_2SO_4 until its specific gravity is 1.347 Excess of concentration of the acid should be avoided, since the acid decomposes under this condition.

$$H_2S_2O_6 \xrightarrow{\text{Decomposition}} H_2SO_4 + SO_2$$

Dithionic acid exists in solution only. The acid decomposes on concentrating its aqueous solution above a specific gravity of 1.347 into H_2SO_4 and SO_2. The acid is remarkably stable towards oxidising agents. On hydrolysis $H_2S_2O_6$ gives H_2SO_4 and H_2SO_3.

$$H_2S_2O_6 + H_2O \longrightarrow H_2SO_4 + H_2SO_3$$

Dithionates ($S_2O_6^{2-}$).

Although $H_2S_2O_6$ has been shown to be *dibasic* by conductivity measurement of its sodium salt, it gives only one type of salts, called *dithionates* ($S_2O_6^{2-}$). Acid thionates (*i.e.* $NaHS_2O_6$) are *unknown*.

Dithionates can be prepared by decomposing BaS_2O_6 solution with a metal sulphate or metal carbonate, filtering off $BaSO_4$ or $BaCO_3$ and crystallising. Dithionates are also prepared by the electrolytic oxidation of neutral or alkaline solutions of sulphites.

$$2SO_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

All dithionates are soluble in H_2O and mostly crystallise with H_2O. The dithionates of alkaline earth metals are very stable and their solutions may be boiled without decomposition. Dithionates of heavy metals are not so stable. Dithionates also decompose on heating, *e.g.*

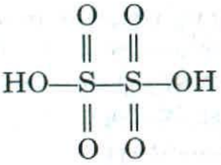
$$K_2S_2O_6 \xrightarrow{\Delta} K_2SO_4 + SO_2$$

Sodium amalgam reduces the solution of a dithionate to the corresponding sulphites, *e.g.*

$$Na_2S_2O_6 + 2Na \longrightarrow 2Na_2SO_3$$

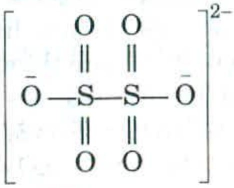
Structure of $H_2S_2O_6$ Molecule and $S_2O_6^{2-}$ Ion.

In $H_2S_2O_6$ two sulphonic acid groups, —SO_2OH are directly linked with each other. Since the acid is dibasic, it has two OH groups linked directly with S-atom. Thus the $H_2S_2O_6$ and $S_2O_6^{2-}$ have the following structures :



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

Dithionic acid
($H_2S_2O_6$)



$$\left[\bar{O}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\bar{O}\right]^{2-}$$

Dithionate ion
($S_2O_6^{2-}$)

The structure of $S_2O_6^{2-}$ ion has approximately *tetrahedral bond angles* about each sulphur atom. The S—O bond distance is 1.43 Å as compared to 1.44 Å in SO_4^{2-} ion. The short bond length suggests considerable double bond character in $S_2O_6^{2-}$ ion.

Polythionic Acids ($H_2S_nO_6$)

Preparation.

Polythionic acids are prepared by various methods. The following methods are, however, important.

1. By the action of sulphur chlorides on sulphites (SO_3^{2-}) and thiosulphates ($S_2O_3^{2-}$) in etheral solution.

$$SCl_2 + 2SO_3^{2-} \longrightarrow \underset{\text{(tri)}}{S_3O_6^{2-}} + 2Cl^-$$

$$SCl_2 + 2S_2O_3^{2-} \longrightarrow \underset{\text{(penta)}}{S_5O_6^{2-}} + 2Cl^-$$

$$S_2Cl_2 + 2SO_3^{2-} \longrightarrow \underset{\text{(tetra)}}{S_4O_6^{2-}} + 2Cl^-$$

$$S_2Cl_2 + 2S_2O_3^{2-} \longrightarrow \underset{\text{(tetra)}}{S_4O_6^{2-}} + 2Cl^-$$

2. By passing H_2S through a saturated aqueous solution of SO_2. When H_2S gas is passed very slowly through a solution of SO_2 kept cooled by *ice, Wakenroder solution* is obtained. This solution contains a mixture of polythionic acids, suspended and colloidal sulphur, $H_2S_2O_3$ etc. and hence can be used to prepare polythionic acids. The following mechanism for the formation of polythionic acids has been suggested by Stawrn (1944).

$$H_2S + H_2SO_3 \longrightarrow H_2S_2O_2 + H_2O$$

$$H_2S_2O_2 + 2H_2SO_3 \longrightarrow H_2S_4O_6 + 2H_2O$$

$$2H_2S + H_2SO_3 \longrightarrow 3H_2O + 3S\downarrow$$

$$H_2S_4O_6 + H_2SO_3 \longrightarrow H_2S_2O_3 + H_2S_3O_6$$
$$H_2S_2O_3 + 2H_2S_2O_3 \longrightarrow H_2S_6O_6 + 2H_2O$$

In less acidic solutions, $H_2S_6O_6$ undergoes decomposition as follows :

$$H_2S_6O_6 \longrightarrow H_2S_5O_6 + S\downarrow$$
$$H_2S_5O_6 + H_2SO_3 \longrightarrow H_2S_4O_6 + H_2S_2O_3$$

3. Specific methods for the preparation of individual polythionic acids. Preparation of individual polythionic acids by specific methods is done by the following reactions :

(*a*) $\mathbf{H_2S_3O_6}$: $\underset{\text{(solution)}}{K_2S_3O_6} + H_2SiF_6 \rightleftharpoons \underset{\text{(soluble)}}{H_2S_3O_6} + \underset{\text{(insoluble)}}{K_2SiF_6}$

(*b*) $\mathbf{H_2S_4O_6}$: $\underset{\text{(solution)}}{BaS_4O_6} + H_2SO_4 \longrightarrow \underset{\text{(insoluble)}}{BaSO_4} + \underset{\text{(soluble)}}{H_2S_4O_6}$

(c) $\mathbf{H_2S_5O_6}$: $5S_2Cl_2 + 6H_2O \xrightarrow{\text{Hydrolysis}} H_2S_5O_6 + 10HCl + 5S$

(*d*) $\mathbf{H_2S_6O_6}$: $2K_2S_2O_3$ (in acetone) $+ S_2Cl_2 \xrightarrow{-78°C} H_2S_6O_6 + 2KCl$

Properties

(*i*) **Decomposition.** The free polythionic acids exist only in solution. The solutions of $H_2S_4O_6$ and $H_2S_5O_6$ are sufficiently stable to be concentrated, without decomposition, upto a density of 1.5. On keeping, the solutions of all polythionic acids decompose to give H_2SO_4, SO_2 and sulphur as the final products.

For example :

$$H_2S_3O_6 \longrightarrow H_2SO_4 + SO_2 + S$$
$$H_2S_4O_6 \longrightarrow H_2SO_4 + SO_2 + 2S$$
$$H_2S_5O_6 \longrightarrow H_2SO_4 + SO_2 + 3S$$

In general the decomposition may be shown as :

$$H_2S_nO_6 \longrightarrow H_2SO_4 + SO_2 + (n-2)S.$$

(*ii*) **Change in stability.** The stability of solutions of polythionic acids is increased by the addition of a Little mineral acid while the same is diminished in the presence of free alkali.

(*iii*) **Dibasic nature.** All the polythionic acids are dibasic but the acid salts of these acids have not been prepared so far.

(*iv*) **Stability.** The alkali polythionates are quite stable in aqueous solution; those of alkaline earth metals are less so. The heavy metal polythionates, as a rule, are unstable.

(*v*) **Solubility.** Polythionates are all soluble in water. However, polythionates of Ag and Hg are insoluble. Of the potassium salts which are the best known, the trithionate is the most soluble, the hexathionate comes next; while tetra- and pentathionates are the least soluble, almost insoluble. The difference in solubilities of potassium salts may be utilised in the separation of a mixture of polythionic acids.

***(vi)* Action of oxidising agent.** Aqueous solution of all polythionates are converted into sulphates when treated with oxidising agents. For example :

$$S_3O_6^{2-} + 2H_2O + 4O \longrightarrow SO_4^{2-} + 2H_2SO_4$$

$$S_4O_6^{2-} + 3H_2O + 7O \longrightarrow SO_4^{2-} + 3H_2SO_4$$

In general :

$$S_nO_6^{2-} + (n-1)\ H_2O + (3n-5)\ O \longrightarrow SO_4^{2-} + (n-1)\ H_2SO_4.$$

***(vii)* Reduction.** These are reduced to thiosulphates on treatment with alkali sulphides. For example :

$$S_3O_6^{2-} + S^{2-} \longrightarrow 2S_2O_3^{2-}$$

$$S_4O_6^{2-} + S^{2-} \longrightarrow 2S_2O_3^{2-} + S$$

$$S_5O_6^{2-} + S^{2-} \longrightarrow 2S_2O_3^{2-} + 2S$$

$$S_6O_6^{2-} + S^{2-} \longrightarrow 2S_2O_3^{2-} + 3S$$

Polythionates, when treated with alkali sulphite, get gradually reduced to give ultimately the trithionate and thiosulphate.

$$S_6O_6^{2-} + SO_3^{2} \longrightarrow S_5O_6^{2-} + S_2O_3^{2-}$$

$$S_5O_6^{2-} + SO_3^{2-} \longrightarrow S_4O_6^{2-} + S_2O_3^{2-}$$

$$S_4O_6^{2-} + SO_3^{2-} \longrightarrow S_3O_6^{2-} + S_2O_3^{2-}$$

***(viii)* Action of aqueous KCN solution.** When treated with KCN in aqueous solution, a trithionate is converted into thiosulphate ($S_2O_3^{2-}$), sulphate (SO_4^{2-}) and free hydrocyanic acid (HCN).

$$S_3O_6^{2-} + 2CN^- + H_2O \longrightarrow S_2O_3^{2-} + SO_4^{2-} + 2HCN$$

Higher polythionates react similarly. The excess of sulphur combines with a further quantity of KCN to form sulphocyanide (CNS^-).

$$S_4O_6^{2-} + 3CN^- + H_2O \longrightarrow S_2O_3^{2-} + SO_4^{2-} + 2HCN + CNS^-$$

$$S_5O_6^{2-} + 4CN^- + H_2O \longrightarrow S_2O_3^{2-} + SO_4^{2-} + HCN + 2CNS^-$$

***(ix)* Action of $Hg_2(NO_3)_2$ and $AgNO_3$.** Polythionates give precipitates with $Hg_2(NO_3)_2$ or $AgNO_3$.

$$S_3O_6^{2-} + Hg_2(NO_3)_2 \longrightarrow \text{Black ppt.}$$

$$S_4O_6^{2-} \text{ or } S_5O_6^{2-} + Hg_2(NO_3)_2 \longrightarrow \text{Yellow ppt.}$$

$S_4O_6^{2-}$ does give any precipitate with $Hg_2(NO_3)_2$ or $AgNO_3$.

***(x)* Action of sodium or potassium amalgam.** With sodium or potassium amalgam, their solutions are reduced to thiosulphate ($S_2O_3^{2-}$)

$$S_3O_6^{2-} + 2Na/Hg \longrightarrow S_2O_3^{2-} + 2Na^+ + SO_3^{2-}$$

$$S_4O_6^{2-} + 2Na/Hg \longrightarrow 2S_2O_3^{2-} + 2Na^+$$

***(xi)* Action of alkali solution.** $S_3O_6^{2-}$ and $S_4O_6^{2-}$, when treated with an aqueous solution of an alkali, decompose into $S_2O_3^{2-}$ and SO_3^{2-}. $S_6O_6^{2-}$, however, gives only $S_2O_3^{2-}$.

$$2S_3O_6^{2-} + 6OH^- \longrightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O$$

$$2S_4O_6^{2-} + 6OH^- \longrightarrow 2S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O$$

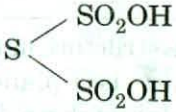
$$2S_5O_6^{2-} + 6OH^- \longrightarrow 5S_2O_3^{2-} + 3H_2O$$

***(xii)* Action of Cu^{2+} ions.** It is only $S_3O_6^{2-}$ which reacts with Cu zone at 70°C to form CuS etc.

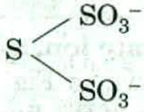
$$S_3O_6^{2-} + 2H_2O + Cu^{2+} \xrightarrow{70°C} CuS + 2SO_4^{2-} + 4H^+$$

Structure of Polythionic Acids and Polythionate Ions.

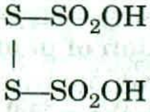
The structure of polythionic acids is obtained by attaching two —SO_2OH groups together through one or more S-atoms. Thus the structure of these acids and the anions derived from them are as given below :



Trithionic
acid
($H_2S_3O_6$)

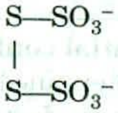


Trthionate
ion
($S_3O_6^{2-}$)



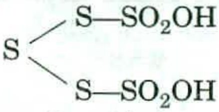
$$\begin{array}{l} S—SO_2OH \\ | \\ S—SO_2OH \end{array}$$

Tetrathionic
acid
($H_2S_4O_6$)

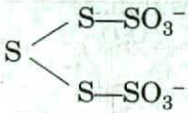


$$\begin{array}{l} S—SO_3^- \\ | \\ S—SO_3^- \end{array}$$

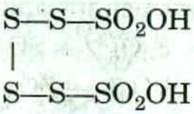
Tetrathionate
ion
($S_4O_6^{2-}$)



Pentathionic
acid
($H_2S_5O_6$)

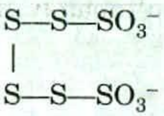


Pentathionate
ion
($S_5O_6^{2-}$)



$$\begin{array}{l} S—S—SO_2OH \\ | \\ S—S—SO_2OH \end{array}$$

Hexathionic
acid
($H_2S_6O_6$)



$$\begin{array}{l} S—S—SO_3^- \\ | \\ S—S—SO_3^- \end{array}$$

Hexathionate
ion
($S_6O_6^{2-}$)

1. Spatial configuration of trithionate ion, $S_3O_6^{2-}$. X-ray analysis of trithionates (*e.g.* $Na_2S_3O_6$, $K_2S_3O_6$ etc.) has shown that the structure of $S_3O_6^{2-}$ ion is as shown in Fig. 36.7. In this structure the two end S-atoms lie in different planes which are inclined at an angle of 99° to each other while the middle S-atom lies on the common axis of the two planes. The SSS bond angle is 108° and both S—S bond lengths are equal to 2.0A°. All the six S—O bond distances are equal to 1.4A°. The disposition of the three O-atoms round each of the end S-atoms is approximately *tetrahedral*.

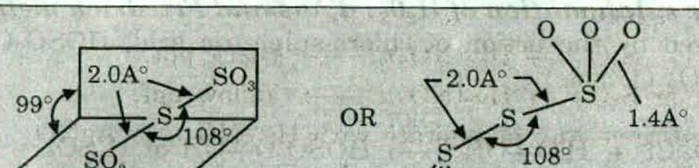


Fig. 36.7. Structure of trithionate ion, $S_3O_6^{2-}$ (Diagrammatic).

2. Spatial configuration of tetrathionate ion, $S_4O_6^{2-}$. X-ray analysis has shown that the structure of this ion is as shown in Fig. 36.8. In this structure the two end S-atoms lie in different planes which are inclined at an angle of 90° to each other while the two middle S-atoms lie on the common axis of the two planes. The bond lengths and bond angles are as shown in the figure. The disposition of the three O-atoms about each of the two end S-atoms is approximately tetrahedral.

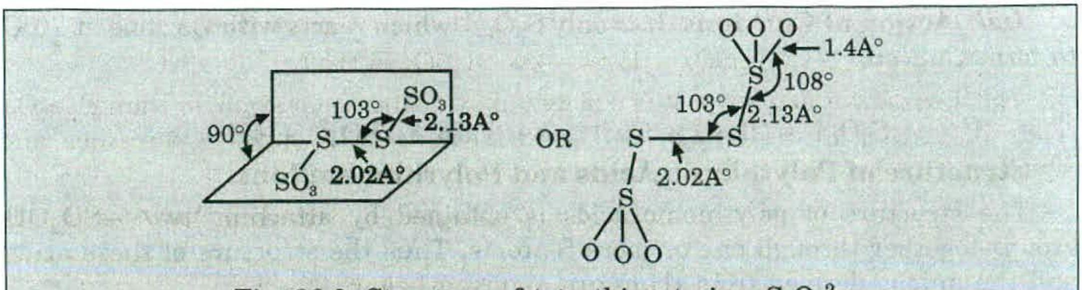


Fig. 36.8. Structure of tetrathionate ion, $S_4O_6^{2-}$.

3. Spatial configuration of pentathionate ion, $S_5O_6^{2-}$. The structure of this ion, as determined by X-ray analysis, is shown in Fig. 36.9. There is a plane of symmetry passing through the middle S-atom of the five-atom sulphur chain. The disposition of the three O-atoms on each of the end S-atom is, as usual, approximately, *tetrahedral.*

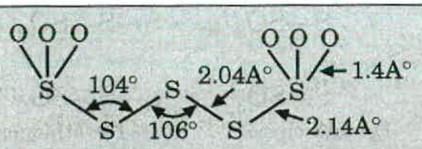


Fig. 36.9. Structure of pentathionate ion, $S_5O_6^{2-}$.

4. Spatial configuration of hexathionate ion, $S_6O_6^{2-}$. The structure of this ion is the same as that of $S_4O_6^{2-}$ and $S_5O_6^{2-}$ ions. The disposition of the three O-atoms about each of the two end S-atoms is approximately tetrahedral.

Peroxy Sulphuric Acids

1. Peroxy Monosulphuric Acid, H_2SO_5.

Preparation. This acid is also called ***Cero's acid.*** It is prepared :

(i) By the sulphonation of H_2O_2: d'Ans and Friedrich method. Pure acid can be prepared by the action of chioro-sulphuric acid, $HOSO_2Cl$ (1 mole) on anhydrous H_2O_2 (1 mole)

$$HOSO_2\boxed{Cl + H}O{-}OH \xrightarrow{-HCl} \underbrace{HOSO_2O{-}OH \text{ or } H_2SO_5}_{\text{Peroxy monosulphuric acid}} + HCl$$

(ii) By the anodic oxidation of H_2SO_4. When conc. H_2SO_4 is submitted to electrolysis in a diaphragm cell at a low temperature, using a small smooth platinum anode and a high current density, a solution of H_2SO_5 is obtained.

$$H_2SO_4 + O \longrightarrow H_2SO_5$$

Properties. (*i*) *Physical state.* Caro's acid in the anhydrous state is a white crystalline solid (m. pt. = 45°C) and hygroscopic. It is stable for some days but gradually loses ozonised oxygen.

(*ii*) *Action of H_2O_2.* On treatment with H_2O_2, it evolves O_2,

$$H_2SO_5 + H_2O_2 \longrightarrow H_2SO_4 + H_2O + O_2$$

(iii) *Hydrolysis.* When diluted with dil. H_2SO_4, it gives H_2O_2

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

(iv) *Oxidising property.* It is a powerful oxidising agent stronger than $H_2S_2O_8$. Thus it oxidises Mn(II), Ag(I), Co(II), Ni(II) and Pb(II) salts to peroxides and liberates Cl_2, Br_2 and I_2 from the respective halides

$$H_2SO_5 + 2AgNO_3 \longrightarrow 2H_2SO_4 + 2HNO_3 + \underset{\text{ppt.}}{Ag_2O_2}$$

$$2KI + H_2SO_5 \longrightarrow K_2SO_4 + H_2O + I_2$$

It also oxidises SO_2 to SO_3, Fe (II) salts to Fe (III) salts, HCl to Cl_2. aniline to nitrosobenzene and nitrobenzene.

(*v*) It carbonises wool and cellulose.

(vi) *Monobasic nature.* No solid salts of H_2SO_5 of M_2SO_5 type are known. However, a solution of $KHSO_5$ is said to be formed by the action of H_2O_2 on $KClSO_3$

$$KClSO_3 + H_2O_2 \longrightarrow KHSO_5 + HCl$$

Thus H_2SO_5 is a *monobasic acid.*

2. Peroxydisulphuric Acid, $H_2S_2O_8$.

Preparation. This acid is also called **Marshall's acid.** It is prepared :

(i) By the sulphonation of H_2O_2 : d'Ans and Friedrich's method. Anhydrous $H_2S_2O_8$ can be prepared by the action of H_2O_2 (1 mole) on chlorosulphuric acid, $ClSO_2.OH$ (2 moles)

$$2ClSO_2OH + 2H_2O_2 \xrightarrow{-2HCl} \underbrace{HOSO_2{-}O{-}O{-}SO_2OH \text{ or } H_2S_2O_8 + 2HCl}_{\text{Per oxydisulphuric acid}}$$

(ii) By the anodic oxidation of H_2SO_4. $H_2S_2O_8$ is obtained, by the electrolysis of H_2SO_4 in cold. About 50% H_2SO_4 is taken in a large glass test tube which is placed in a glass cylinder open at both ends. A spiral of copper wire is wound round this cylinder which acts as a cathode. A fine platinum wire fused in a capillary tube is placed inside the inner tube which acts as an anode. The large glass test tube containing H_2SO_4 is cooled by putting in an ice bath. On passing electric current of high density, $H_2S_2O_8$ is formed in solution at the anode. The reactions taking place at cathode and anode are :

$$\begin{array}{ccc} \textit{Anode} & & \textit{Cathode} \\ HSO_4^- \longleftarrow\!\!\!\longleftarrow & H_2SO_4 & \longrightarrow\!\!\!\longrightarrow H^+ \\ HSO_4^- + HSO_4^- \to H_2S_2O_8 + 2e^- & & H^+ + e^- \to H \\ & & H + H \to H_2 \end{array}$$

Another explanation for the formation of the acid at the anode is that HSO_4^- ions liberated at the anode are oxidised by nascent oxygen that appears at the anode as a result of electrolysis.

$$2HSO_4^- + H_2O + O \longrightarrow H_2S_2O_8 + 2OH^-$$

Properties. ***(i) Physical state.*** It is a colourless, hygroscopic, crystalline compound (m.pt. = 65°C) which is fairly stable at ordinary temperature :

(ii) Decomposition. On heating, $H_2S_2O_8$ decomposes into SO_3 and O_2

$$2H_2S_2O_8 \xrightarrow{\text{heat}} 2H_2SO_4 + 2SO_3 + O_2$$

It is also decomposed by light.

(iii) Hydrolysis. In aqueous solution, $H_2S_2O_8$ is slowly hydrolysed into H_2SO_4 and H_2SO_5.

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$

When distilled with dil. H_2SO_4, it is also hydrolysed but the product is H_2O_2.

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

(iv) The anhydrous acid vigorously reacts with organic compounds.

(v) Oxidising property. The acid and its salts (which are called *perdisulphates*) are strong oxidising agents. The ion-electron equation representing their oxidising property is :

$$M^{2+} + 2H_2O + S_2O_8^{2-} \longrightarrow MO_2 + 4H^+ \; 2SO_4^{2-}$$

or

$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$$

Following examples show the oxidising property of perdisulphates :

(a) They oxidise Mn (II), Ag (I), Pb (II), Co (II) and Ni (II) salts to the corresponding metal peroxides (in presence of an alkali).

$$\begin{aligned} Mn^{2+} + 2H_2O + S_2O_8^{2-} &\longrightarrow MnO_2 + 4H^+ + 2SO_4^{2-} \\ Pb^{2+} + 2H_2O + S_2O_8^{2-} &\longrightarrow PbO_2 + 4H^+ + 2SO_4^{2-} \\ \underset{\text{salts}}{2Ag^+} + 2H_2O + S_2O_8^{2-} &\longrightarrow \underset{\text{peroxides}}{Ag_2O_2} + 2H^+ + 2HSO_4^- \end{aligned}$$

(b) They oxidise Fe (II) salts to Fe (III) salts and Cr (III) salts to chromates (CrO_4^{2-}) even in alkaline medium. Metallic Zn and Cu are oxidised to their sulphates.

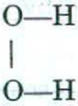
$$\begin{aligned} 2Fe^{2+} + S_2O_8^{2-} &\longrightarrow 2Fe^{3+} + 2SO_4^{2-} \\ Zn^0 + S_2O_8^{2-} &\longrightarrow Zn^{2+} + 2SO_4^{2-} \end{aligned}$$

(c) They liberate Cl_2, Br_2 and I_2 from the solution of the corresponding halide and even oxidises free I_2 to iodic acid and bleaches indigo. The bleaching of indigo and liberation of I_2 from an iodide proceeds slowly.

$$\begin{aligned} 2Cl^- + S_2O_8^{2-} &\longrightarrow Cl_2 + 2SO_4^{2-} \\ 2I^- + S_2O_8^{2-} &\longrightarrow I_2 + 2SO_4^{2-} \\ I_2 + 6H_2O + 5S_2O_8^{2-} &\longrightarrow 2IO_3^- + 10SO_4^{2-} + 12H^+ \end{aligned}$$

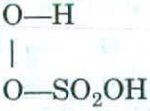
Structure of Peroxysulphuric Acids and Peroxysulphate Ions.

These acids can be regarded as being obtained from H_2O_2 by the replacement of one or both H-atoms by sulphonic acid group, $-SO_2OH$. Thus, these acids can be represented as :



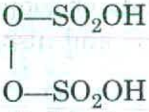
$$\begin{array}{l} O\text{—}H \\ | \\ O\text{—}H \end{array}$$

Hydrogen peroxide
(H_2O_2)



$$\begin{array}{l} O\text{—}H \\ | \\ O\text{—}SO_2OH \end{array}$$

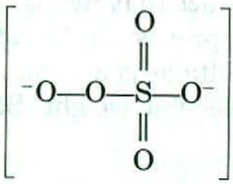
Permonosulphuric acid
or Caro's acid
(H_2SO_5)



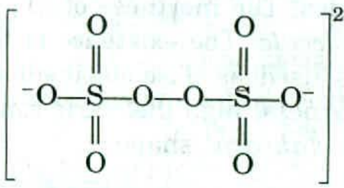
$$\begin{array}{l} O\text{—}SO_2OH \\ | \\ O\text{—}SO_2OH \end{array}$$

Perdisulphuric acid
or Marshall's acid
($H_2S_2O_8$)

Permonosulphate (SO_5^{2-}) and perdisulphate ($S_2O_8^{2-}$) ions have the following structures :



Permonosulphate ion, SO_5^{2-}



Perdisulphate ion, $S_2O_8^{2-}$

X-ray anlysis of $(NH_4)_2S_2O_8$ and $Cs_2S_2O_8$ has shown that $S_2O_8^{2-}$ ion consists of two SO_4 tetrahedra joined together by a covalent bond. The S—O bond distance (= 1.50 A°) is short. The short S—O bond distance indicates a high degree of double bond character.

Distinction Between H_2O_2 and Peroxysulphuric Acids.

The distinction between H_2O_2 and peroxy sulphuric acids can be made by the following tests :

1. $KMnO_4$ test. When H_2O_2 is added to a solution of $KMnO_4$ acidified with H_2SO_4, $KMnO_4$ decolorises and O_2 is evolved. Persuiphuric acids do not react.

2. $K_2Cr_2O_7$ test. When H_2O_2 is added to a solution of $K_2Cr_2O_7$, acidified with dil. H_2SO_4 and to which a little diethyl ether has been added, bright blue *chromium peroxide,* CrO_5 is formed that passes into etheral layer on gentle shaking. Persulphuric acids do not show this test.

3. $Ti(SO_4)_2$ test. H_2O_2 reacts with an acidified solution of $Ti(SO_4)_2$ to give a yellow or orange-red colouration, due to the formation of *pertitanic acid*, $TiO_2.xH_2O$. Persulphuric acids do not show this reaction.

4. Aniline test. Coro's acid (H_2SO_5) forms nitroso benzene and nitrobenzene with aniline while Marshall's acid ($H_2S_2O_8$) gives aniline black. H_2O_2 does not show this reaction.

Halides

Sulphur forms a number of halides. Out of these, sulphur hexafluoride, SF_6 is the most important. It is prepared by allowing sulphur to burn spontaneously in F_2. The gaseous SF_6 so formed is usually mixed with low fluorides of sulphur and hence the resulting gaseous mixture of fluorides is liquified at —80°C and then fractionally distilled, separating the lower fluorides by caustic potash solution. SF_6 is a colourless and odourless gas (m.pt. = 50.8°C and b. pt. = + 68.8°C). It is chemically inert like N_2 and hence remains unaffected by heat. It also remains undecomposed by water, acids or alkalies. Even fused caustic potash and ignited lead chromate or copper have no effect on it. It is decomposed by molten (boiling) Na at 250°C and also by H_2S.

$$SF_6 + 8Na \longrightarrow Na_2S + 6NaF$$

$$SF_6 + 3H_2S \longrightarrow 6HF + 4S$$

It is also decomposed by H_2 at 400°C and by sparking with H_2 or O_2. In stability and non-reactivity, SF_6 resembles CCl_4 and differs from all other non-metallic halides. The inertness of SF_6 is due to the fact that SF_6 is a *covalently saturated molecule*. The existence of this compound proves the hexacovalency of S-atom. It is used as gaseous insulator in high voltage generators due to its chemical inertness, high dielectric constant and molecular weight. SF_6 molecule has *regular octahedral* shape.

Oxyhalides

Sulphur forms a number of oxyhalides. Here we shall discuss only thionyl chloride ($SOCl_2$) and sulphonyl chloride (SO_2Cl_2).

1. Thionyl Chloride, $SOCl_2$.

Preparation. It is prepared by adding sulphur into Cl_2O at –12°C or by the action of SO_3 on S_2Cl_2 at 75°–80° (*Commercial method*).

$$S + Cl_2O \xrightarrow{-12^\circ C} SOCl_2$$

$$SO_3 + C_2Cl_2 \xrightarrow{72^\circ\text{–}80^\circ} SOCl_2 + SO_2 + S$$

Properties. It is a colourless, pungent smelling liquid of density 1677 (at 0°C) b.pt. = 78°C and m.pt. = – 99.5°C. It fumes in moist air and gets decomposed by H_2O forming H_2SO_3 and HCl. Organic compounds containing OH groups react with $SOCl_2$ and OH group is replaced by Cl atom.

$$SOCl_2 + 2H_2O \longrightarrow H_2SO_3 + 2HCl$$

$$\underset{\substack{\text{Organic}\\ \text{compound}}}{ROH} + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

It reacts with KBr, forming thionyl bromide, $SOBr_2$

$$SOCl_2 + 2KKr \longrightarrow SOBr_2 + 2KCl$$

$SOCl_2$ reacts with SbF_3 in presence of $SbCl_5$ (Swart's reagent) to form thionyl fluoride, SOF_2

$$3SOCl_2 + 2SbF_3 \xrightarrow{\substack{\text{In presence}\\ \text{of } SbCl_5}} 3SOF_2 + 2SbCl_3$$

Uses. It is used a reagent in organic chemistry to replace OH groups present in organic compounds by Cl atom.

Structure. In $SOCl_2$ molecule S-atom is sp^3 hbridised. Due to the presence of one lone pair of electrons on S-atom, the molecule has distorted tetrahedral shape, *i.e., trigonal pyramidal shape*. This shape contains two Cl^- and one O-atoms in a traingle (Fig. 36.10). S—O π bond is *d—p* π bond.

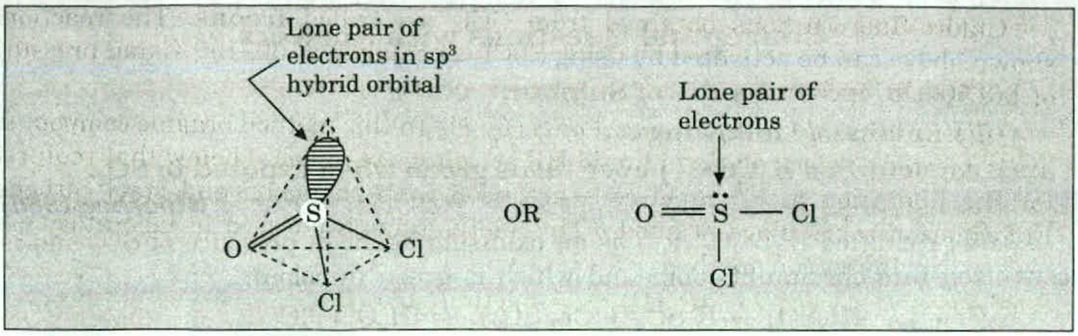


Fig. 36.10. Trigonal pyramidal shape of thionyl chloride, $SOCl_2$.

2. Sulphonyl Chloride, SO_2Cl_2.

Preporation. This compound is also called ***sulphuryl chloride*** and is formed by the direct combination of SO_2 and Cl_2 in sunlight or in the presence of catalyst like camphor, charcoal or acetic anhydride.

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

Properties. It is a white fuming liquid of specific gravity of 1.667 at 20°C. It boils at 69.1°C without decomposition; the vapour is much dissociated at 330°C.

$$SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$$

With ice-cold water it gives a crystalline hydrate, $SO_2Cl_2.15H_2O$.

When warmed with water, it is first hydrolysed to chlorosulphuric acid, $(OH)SO_2Cl$ and then to H_2SO_4.

$$\begin{array}{lcl} SO_2Cl_2 + H_2O & \longrightarrow & (OH)SO_2Cl + HCl \\ (OH)SO_2Cl + H_2O & \longrightarrow & SO_2(OH)_2 \text{ or } H_2SO_4 + 3HCl \\ \hline SO_2Cl_2 + 2H_2O & \longrightarrow & SO_2(OH)_2 \text{ or } H_2SO_4 + 3HCl \end{array}$$

In benzene, SO_2Cl_2 reacts with NH_3 to form sulphamide, $SO_2(NH_2)_2$. With CH_3COONa, it forms acetyl chloride, CH_3COCl.

Uses. Its solution in petrol is used in making the wool unshrikable. It is used as a chlorinating agent in organic chemistry, *i.e.*, it is used for introducing sulphonic acid group.

Structure. In SO_2Cl_2 molecule S-atom is sp^3 hybridised, and hence the molecule has *tetrahedral shape* (See Fig. 36.11). It may be noted that one S—O π bond is *p–p* π bond while the other S—O bond is *d—p* π bond.

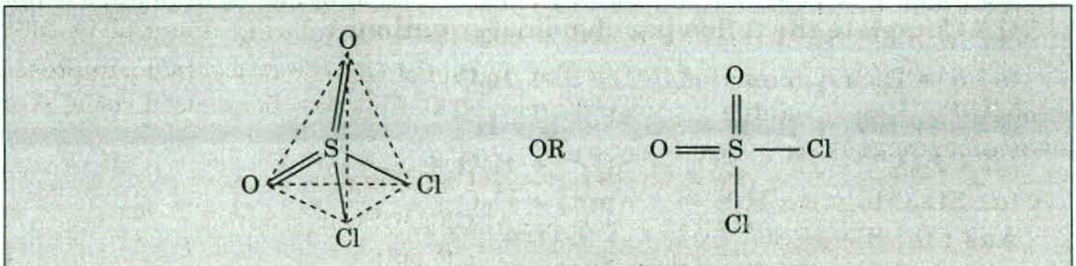


Fig. 36.11. Tetrahedral shape of sulphuryl chloride or sulphonyl chloride, SO_2Cl_2.

Conceptual Questions with Answers

[A] Questions on Oxides of Sulphur.

Q.1 Explain the following :

(*i*) An acidified $K_2Cr_2O_7$ paper turns green when exposed to SO_2. ***(Roorkee 1986)***

Ans : Acidified $K_2Cr_2O_7$ acts as an oxidising agent in presence of SO_2 and is converted into chromium compound which is green in colour.

$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

$3SO_2 + 3O + 3H_2O \rightarrow 3H_2SO_4$

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$

(*ii*) SO_2 acts as a bleaching agent.

Ans : SO_2 in presence of moisture is oxidised to H_2SO_4 liberating nascent hydrogen. The nascent hydrogen bleaches the coloured substance.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$$

Coloured substance + 2H → Colourless

(*iii*) SO_2 does not bleach dry flowers.

Ans : Only in presence of moisture, the nascent hydrogen responsible for bleaching (redcution) is produced.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$$

Coloured flower + H → Colourless flower

If H_2O or moisture is not present, nescent hydrogen will not be prodcued and hence flowers will not be bleached.

(*iv*) SO_2 is neither conbustible nor helps in burning, yet burning Mg continues to burn in it.

Ans : The heat of reaction is suffecient to dissociate SO_2 into S and free O_2. O_2 thus obtained burns Mg.

Q.2 How is SO_2 obtained from H_2SO_4 ?

Ans : SO_2 can be obtained by heating Cu-turnings with conc. H_2SO_4 or by boiling sulphur with conc. H_2SO_4.

$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2$; $S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$

Q.3 Complete the following chemical equations :

(*a*) $S + H_2SO_4$ (*conc.*) $\xrightarrow{\Delta}$ ... + H_2O

(*b*) $I_2 + SO_2 + H_2O \rightarrow SO_4^{2-}$ + ... + H^+

(*c*) $Cr_2O_7^{2-} + H^+ + SO_2 \rightarrow SO_4^{2-} + H_2O$ + ...

(*d*) SO_2(Moist) + $H_2S \rightarrow$ ... (ppt) + H_2O

Ans : (*a*) $S + H_2SO_4$ (conc.) $\rightarrow 3SO_2 + 2H_2O$

(*b*) $I_2 + SO_2 + 2H_2O \rightarrow SO_4^{2-} + 2I^- + 4H^+$

(*c*) $Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow 3SO_4^{2-} + H_2O + 2Cr^{3+}$

(*d*) SO_2(Moist) + $2H_2S \rightarrow 3S$(ppt) + $2H_2O$

Q.4 Give exampels to show that :

(*i*) SO_2 acts as a reducing agent (RA).

Ans : $Cl_2 + 2H_2O + SO_2 \rightarrow H_2SO_4 + 2HCl$

(Cl = 0) (S = +4) (S = +6) (Cl = –1)

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

(Fe = +3) (S = +4) (S = +6) (Fe = +2)

In both the reactions, since SO_2 is oxidised to H_2SO_4, SO_2 acts as a RA.

(*ii*) SO_3 is an anhydride of H_2SO_4.

Ans : Since the combination of SO_3 with H_2O gives H_2SO_4, this oxide is the anhydride of H_2SO_4

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Q.5 H_2S acts only as a reducing agent (RA) but SO_2 acts both as a reducing agent as well as an oxidising agent (O.A). Expalin why ?

(***Roorkee 1986***)

Ans : Minimum O.N of S-atom in – 2 and maximum O.N. of this atom is +6.

In H_2S, O.N. of S-atom is equal to – 2. When H_2S acts as a reducing agent, it gets oxidised and hence O.N. of S-atom increases from – 2 to some higher O.N. Thus H_2S can easily act as a reducing agent. If H_2S acts as an O.A., O.N. of S-atom should decrease from – 2 to some lower O.N. which is not possible. Thus H_2S cannot act as an O.A.

In SO_2, O.N. of S-atom is equal to + 4. When SO_2 acts as a R.A., it gets oxidised and hence O.N. of S-atom increases from + 4 to higher O.N. (= + 6) which is possible. Thus SO_2 can act as a RA. When SO_2 acts as an OA, it gets reduced and hence O.N. of S-atom decreases from + 4 to lower O.N. (= + 2). This is also possible. Thus SO_2 can also act as an OA. The above discussion clearly indicates SO_2 can act both as a RA and as an OA but H_2S can act only as a RA.

[B] Questions an Oxy acids of Sulphur.

1. Explain the following :

(*i*) The value of K_{a2} is less than that of K_{a1} for H_2SO_4.

Ans : H_2SO_4 is a dibasic acid. Hence it ionizes in two stages and has two dissociation constants.

(*i*) $H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$; $K_{a1} > 10$

(*ii*) $HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$; $K_{a2} = 1.2 \times 10^{-2}$

The value of K_{a2} is less than K_{a1} because the negatively charged HSO_4^- ion has much less tendency to donate a proton to H_2O as compared to neutral H_2SO_4.

(*ii*) (*a*) In the contact process for the manufacture of H_2SO_4, some amount of sulphuric acid is used as a starting material. Explain briefy.

(*b*) What is the catalyst used for oxidation of SO_2 to SO_3 ?

Ans : (*a*) In contact process, H_2SO_4 is used initially to absorb SO_3 to form oleum.

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7 \ (\textit{Oleum})$$

Oleum is then diluted with calculated amount of water to get H_2SO_4 of desired concentration. It may be noted that SO_3 is not directly absorbed in water to form H_2SO_4 because it forms a dense fog of H_2SO_4 which does not condens easily.

(*b*) V_2O_5 is used as catylst for oxidation of SO_2 to SO_3.

(*iii*) H_2S can not be dried by passing it through conc. H_2SO_4.

Ans : H_2S can not be dried by passing it through conc. H_2SO_4, since it is oxidised by H_2SO_4 to S.

$$H_2SO_4 \rightarrow H_2O + SO_2 + O$$
$$H_2S + O \rightarrow H_2O + S$$
$$\overline{\underset{(OA)}{H_2SO_4} + \underset{(RA)}{H_2S} \rightarrow 2H_2O + SO_2 + S}$$

(*iv*) In the manufacture of H_2SO_4 by contact process, SO_3 is not directly dissolved in H_2O.

Ans : SO_3 reacts with H_2O to form H_2SO_4 which is not easily condensed but escapes in the atmoshphere. SO_3 is, therefore, dissolved in H_2SO_4 (not in H_2O) to form oleum ($H_2S_2O_7$) which, on dilution, gives H_2SO_4

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7 \ (oleum)$$
$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4.$$

(*v*) For the dilution of conc. H_2SO_4, water should not be added to conc. H_2SO_4.

Ans : Conc. H_2SO_4 has great affinity for H_2O molecules. During addition of water to conc. H_2SO_4, large amount of heat released rises the temperature suddenly and hence bumping takes place. To avoid any accident due to bumping, water should not be added to the acid. Instead, we should add acid to water with constant stirring.

(*vi*) Conc. H_2SO_4 cannot be used for drying H_2.

Ans : H_2 is oxisised by H_2SO_4 to H_2O ($H_2SO_4 + H_2 \rightarrow 2H_2O + SO_2$). Sometimes H_2O formed as above is absorbed by H_2SO_4 and heat is released. This heat ignites H_2.

(*vii*) $KMnO_4$ should not be dissolved in conc. H_2SO_4.

Ans : Mn_2O_7 is formed in the reaction between $KMnO_4$ and H_2SO_4. Mn_2O_7 is unstable and explosive in nature.

$$2KMnO_4 + 2H_2SO_4 \rightarrow K_2SO_4 + (MnO_3)_2SO_4 + 2H_2O$$
$$(MnO_3)_2SO_4 + H_2O \rightarrow Mn_2O_7 + H_2SO_4$$

(*viii*) H_2SO_4 has high boiling point and viscosity.

Ans : High b.pt. and viscosity of H_2SO_4 is due to the fact that many H_2SO_4 molecules unit together by intermolecular H-bonding and a cluster is formed. It is due to the formation of a cluster that H_2SO_4 has high b.pt. and high viscosity.

(*ix*) A fresh strain of I_2 is generally washed away with hypo solution.

Ans : Hypo solution ($Na_2S_2O_3$) reduces I_2 to colourless NaI and , therefore, fresh strain of I_2 is washed away.

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

or $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Q.2 State with balanced equation what happens when :

(*i*) Pot. ferrocyanide is heated with conc. H_2SO_4. (***I.I.T. 1988***)

Ans : CO is evolved.

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

(*ii*) A mixture of pot. chlorate, oxalic acid and H_2SO_4 is heated. (***I.I.T.1985***)

Ans : Potassium chlorate is reduced while oxalic acid is oxidised.

$$KClO_3 + H_2SO_4 \rightarrow KHSO_4 + HCl + 3O$$
$$\underline{3H_2C_2O_4 + 3O \rightarrow 6CO_2 + 3H_2O}$$
$$KClO_3 + 3H_2C_2O_4 + H_2SO_4 \rightarrow KHSO_4 + HCl + 6CO_2 + 3H_2O$$

(*iii*) H_2SO_4 is heated with PCl_5.

Ans : $H_2SO_4 + PCl_5 \xrightarrow{\Delta} SO_2Cl_2 + POCl_3 + {}_2HCl$

(*vi*) KI is hetaed with conc. H_2SO_4.

Ans : $2KI + H_2SO_4 \rightarrow K_2SO_4 + 2HI$

$$\underline{2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O}$$
$$\underset{(RA)}{2KI} + \underset{(OA)}{2H_2SO_4} \rightarrow K_2SO_4 + I_2 + SO_2 + 2H_2O$$

In this reaction KI is oxidised to I_2 and H_2SO_4 is reduced to SO_2.

(*v*) Concentrated sulphuric acid is added to a mixture of sodium chloride and manganese dioxide.

Ans : $2NaCl(s) + 2H_2SO_4(aq) + 2MnO_2(s) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + Cl_2(g)$

(*vi*) Sugar turns black on addition of conc. H_2SO_4.

Ans : Conc. H_2SO_4 has great affinity for water molecules, *i.e.*, it acts as a dehydrating agent. When in contact with sugar, all water molecules are taken up and carbon is left behind.

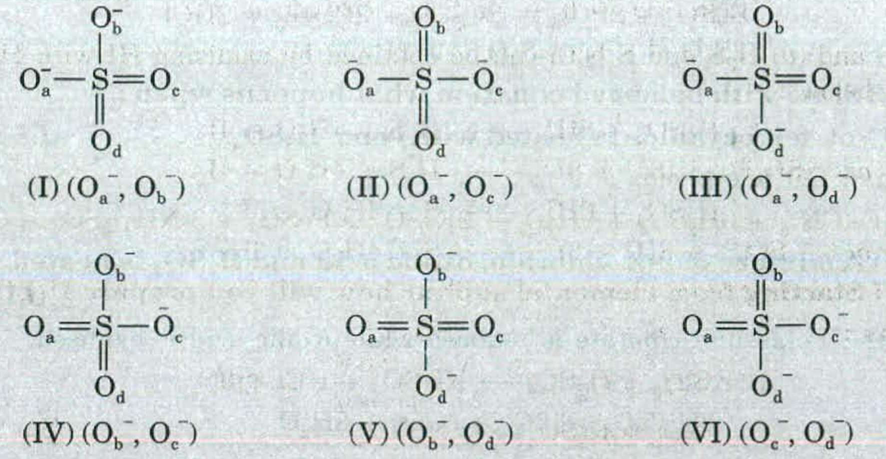
$$C_{12}H_{22}O_{11} \xrightarrow{\text{Conc. } H_2SO_4} 12C + 11H_2O$$

Q.3 Determine the bond order (B.O.) of SO_4^{2-} ion.

Ans : We know that SO_4^{2-} ion is a reasonance hybrid of the six resonating structures shown in Fig. 36.12. In these structures four O-atoms have been designated as O_a, O_b, O_c and O_d. Obviously :

B.O. of S–O_a bond SO_4^{2-} ion.

$$= \frac{1+1+1+2+2+2}{6} = \frac{9}{6} = \mathbf{1.5\ (Ans)}$$


(I) (O_a^-, O_b^-) (II) (O_a^-, O_c^-) (III) (O_a^-, O_d^-)

(IV) (O_b^-, O_c^-) (V) (O_b^-, O_d^-) (VI) (O_c^-, O_d^-)

Fig. 36.12. Various resonating structures of SO_4^{2-} ion.

Q.4 H_2SO_4 acts as an acid, as an oxidising agent and as a dehydrating agent. In which way does it behave when it acts on :

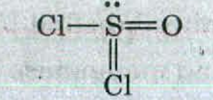
(*a*) Glucose **(*b*) Sulphur** **(*c*) $CaCO_3$** **(*d*) Cu**

(*e*) HCOOH **(*f*) HI** **(*g*) NaOH** **(*h*) C.**

Ans : (*a*) Dehydrating agent (*b*) Oxidising agent (*c*) An acid (*d*) Oxidising agent (*e*) Dehydrating agent (*f*) Oxidising agent (*g*) An acid (*h*) Oxidising agent.

Q.5 Why is sulphurous acid a reducing agent (RA)?

Ans : The structure of sulphurous acid molecule (H_2SO_3) is given in the margin in a box. This structure shows that the central S-atom has a *lp* of electrons. It is due to the presence of this *lp* of electrons that H_2SO_3 can easily be oxidised to H_2SO_4. Consequently H_2SO_3 can act as a RA.


Structure of $SOCl_2$ molecule

$$\underset{(S\,=\,+4)}{H_2SO_3} + H_2O + \underset{(Br\,=\,0)}{Br_2} \longrightarrow \underset{(Br\,=\,-1)}{2HBr} + \underset{(S\,=\,+6)}{H_2SO_4}$$

Q.6 How you will obtain the following from sulphuric acid ?

(*i*) SO_2 **(*ii*) SO_3** **(*iii*) SO_2Cl_2** **(*iv*) H_2S** **(*v*) S.**

Ans : (*i*) (*a*) SO_2 is obtained by heating copper with conc. H_2SO_4.

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

(*b*) It can also the obtained by boiling sulphur with conc. H_2SO_4.

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

(*ii*) H_2SO_4 when treated with P_2O_5 loses water and forms SO_3.

$$H_2SO_4 \xrightarrow{P_2O_5} SO_3 + H_2O$$

$$P_2O_5 + H_2O \longrightarrow 2HPO_3$$

$$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$$

(*iii*) SO_2Cl_2 is formed when conc. H_2SO_4 is treated with excess of PCl_5.

$$H_2SO_4 + 2PCl_5 \rightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

(*iv*) and (*v*) H_2S and S both can be obtained by oxidising HI with H_2SO_4 as shown below :

(*a*) $H_2SO_4 + 8HI \longrightarrow H_2S + 4H_2O + 4I_2$

or $SO_4^{2-} + 10H^+ + 8I^- \longrightarrow H_2S + 4H_2O + 4I_2$

(*b*) $H_2SO_4 + 6HI \longrightarrow S + 4H_2O + 3I_2$

or $SO_4^{2-} + 8H^+ + 6I^- \longrightarrow S + 4H_2O + 3I_2$

Q.7 Starting from elemental suphur how will you prepare H_2SO_4 ?

Ans : $S + O_2 \longrightarrow SO_2$

$$SO_2 + O_2 \xrightarrow[\text{2 bar pressure}]{V_2O_5,\ 720\ K} 2SO_3$$

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Q.8 From the reactions given below, identity (A), (B), (C) and (D) and write their formulae.

(A) + dil. $H_2SO_4 + K_2Cr_2O_7 \longrightarrow$ (B) (Green coloured)

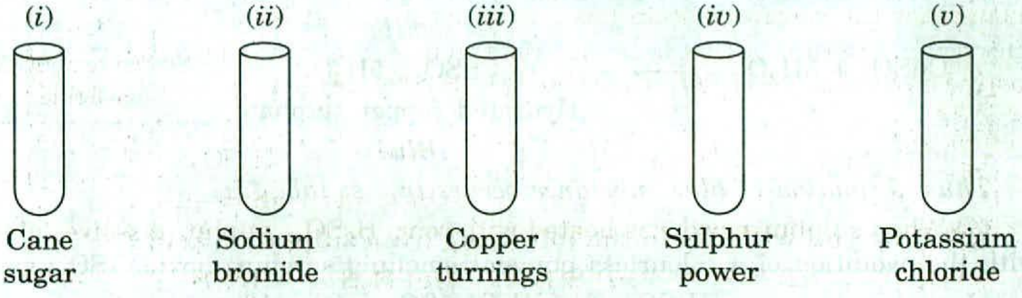
(A) + dil. H_2SO_4 + (C) $\longrightarrow MnSO_4$

(A) + $O_2 \xrightarrow{H_2O}$ (D)

(D) + $BaCl_2 \longrightarrow$ White ppt. (Roorkee 1987)

Ans : (A) = Na_2SO_3; (B) = $Cr_2(SO_4)_3$; (C) = $KMnO_4$; (D) = Na_2SO_4

Q.9 Concentrated sulphuric acid is added to each of the following test tubes labelled (*i*) to (*v*).



Identify in which of the above test tubes, the following change will be observed. Support your answer with the help of a chemical change.

(*a*) formation of black substance

(*b*) evolution of brown gas

(*c*) formation of brown substance which on dilution becomes blue

(*d*) disappearance of yellow powder along with the evolution of a colourless gas

(*e*) evolution of colourless gas.

Ans : (*a*) When conc. H_2SO_4 reacts with cane sugar, water is removed from cane sugar and sugar charcoal (black substance) is obtained. In this reaction conc. H_2SO_4 acts as a dehydrating a gent.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Conc.}H_2SO_4} \underset{\substack{\text{Sugar charcoal}\\(\textit{black substance})}}{12C} + \underset{\text{Water}}{11H_2O}$$

Thus we see that in the reaction occuring in test tube (i) the formation of a black substance (i.e. sugar charcoal) takes place.

(*b*) When sodium bromide is heated with conc. H_2SO_4, a brown gas (Br_2) is obtained. In fact, first HBr is produced. Since HBr is a moderate reducing agent, it reduces H_2SO_4 to SO_2 and is itself oxidised to bromine gas (Br_2). Conversely, H_2SO_4 is a moderate oxidising agent, it oxidises HBr to Br_2

$$\begin{array}{l} 2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBr \\ 2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O \\ \hline \underset{\text{Sod. bromide}}{2NaBr} + 2H_2SO_4\,(\textit{conc.}) \xrightarrow{\text{Heat}} Na_2SO_4 + \underset{\substack{\text{Bromine}\\(\textit{Brown gas})}}{Br_2} + \underset{\substack{\text{Sulphur}\\\text{dioxide}}}{SO_2} + 2H_2O \end{array}$$

Thus, evolution of brown gas occurs in test tube (ii)

(*c*) When copper turnings are heated with conc. H_2SO_4, first a brownish substance (presumably a mixture of unreacted copper turnings and colourless anhydrous copper sulphate) is formed along with evolution of pungent smelling sulphur dioxide (SO_2) gas. The initially formed brown substance on dilution turns blue due to the formation of hydrated copper sulphate while copper turnings remain undissolved.

$$Cu + 2H_2SO_4 \xrightarrow{\text{Heat}} \underset{\substack{\text{Anhydrous copper sulphate}\\(\textit{white})}}{CuSO_4} + SO_2 + 2H_2O$$

$$CuSO_4 + 5H_2O \longrightarrow \underset{\substack{\text{Hydrated copper sulphate}\\(\textit{Blue})}}{CuSO_4 \cdot 5H_2O}$$

Thus, formation of blue substance occurs in test tube (iii)

(*d*) When sulphur powder is heated with conc. H_2SO_4, sulphur dissolves along with the evolution of a colourless pungent smelling sulphur dioxide (SO_2) gas.

$$\begin{array}{l} H_2SO_4 \longrightarrow H_2O + SO_2 + O] \times 16 \\ S_8 + 16O \longrightarrow 8SO_2 \\ \hline \underset{\substack{\text{Sulphur}\\(\textit{Yellow powder})}}{S_8} + 16\,H_2SO_4 \longrightarrow \underset{\substack{\text{Sulphur dioxide}\\(\textit{Colourless pungent}\\\textit{smellling gas})}}{24SO_2} + 16\,H_2O \end{array}$$

Thus, colourless pungent smelling sulphur dioxide gas is evolved is test tube (iv)

(*e*) When potassium chloride is heated with conc. H_2SO_4, a colourless gas hydrogen chloride (HCl) is produced.

$$\underset{\text{Pot. chloride}}{2KCl} + H_2SO_4\ (conc.) \xrightarrow{\text{Heat}} \underset{\substack{\text{Hydrogen chloride}\\ (\textit{Colourless gas})}}{2HCl} + K_2SO_4$$

It may be noted here that unlike HBr, HCl is not a reducing agent. Therefore, it does not reduce H_2SO_4 to SO_2. Conversely, H_2SO_4 is a moderate oxidising agent. Therefore it does not oxidise HCl to Cl_2.

Thus, evolution of colourless gas occurs in test tube (v)

[C] Questions on Halides and Oxy halides of Sulphur.

Q.1 Explain the following, giving appropriate reasons for your answer.

(*i*) SF_6 is known but SCl_6 is not known.

Ans : Fluorine is a much stronger oxidising agent than chlorine, therefore, it can easily oxidise sulphur to its maximum oxidation state of + 6 and hence forms SF_6. Chlorine, on the other hand, being a weaker oxidising agent can oxidise sulphur at the maximum to its + 4 oxidation state and hence can form SCl_4 but not SCl_6.

$$\underset{(S = 0)}{S} + \underset{(F = 0)}{3F_2} \longrightarrow \underset{(S = +6,\ F = -1)}{SF_6} \quad (\textit{Possible reaction})$$

$$S + 3Cl_2 \longrightarrow SCl_6 \quad (\textit{Not possible})$$

$$\underset{(S = 0)}{S} + \underset{(Cl = 0)}{2Cl_2} \longrightarrow \underset{(S = +4,\ Cl = -1)}{SCl_4} \quad (\textit{Possible reaction})$$

Since Cl^- ion is larger in size than F^- ion, S-atom cannot accomdate large-sized Cl^- ions round it and hence cannot form SCl_6 molecule.

(*ii*) SF_6 is known but SH_6 is not known.

Ans : This can be explained in any of the following two ways :

(*i*) We know that the valence-shell of S-atom ($S = 3s^2\ 3p^2\ 3p^1\ 3p^1$) has only two unpaired electrons ($n = 2$). Now for the formation of SF_6 and SH_6 molecules paired electrons present in 3*s* and one of the three 3*p* orbitals must be made unpaired by promoting them in the vacant 3*d* orbitals so that we get six unpaired electrons. Since F-atom is highly electronegative (F = 4.0), it can easily cause the promotion of electrons of S-atom from the filled 3*s* and 3*p* orbitals to the vacant 3*d* orbitals and thus six unpaired electrons ($n = 6$) are obtained. These six unpaired electrons are used in forming SF_6 molecule.

However, H-atom is less electronegative, even lesser than S-atom (H = 2.20, S = 2.44), it cannot cause the promotion of paired electrons to occupy 3*d* orbitals. Thus S-atom has only two unpaired electrons ($n = 2$) and hence can form only SH_2 and not SH_6.

(*ii*) The formation of SF_6 and SH_6 molecules can be represented by the following chemical equations.

(*a*) $$\underset{(S = 0)}{S} + \underset{(F = 0)}{3F_2} \xrightarrow{\text{Oxidation}} \underset{(S = +\ 6,\ F = -\ 1)}{SF_6} \ (\textit{Possible reaction})$$

(*b*) $$\underset{(S = 0)}{S} + \underset{(H = 0)}{3H_2} \xrightarrow{\text{Reduction}} \underset{(S = -\ 6,\ H = +\ 1)}{SH_6} \ (\textit{Not possible})$$

In reaction (*a*), S (S = 0) is oxidised to SF_6(S = + 6) by F_2 which acts as an oxidising agent. Now since F_2 is the strongest oxidising agent, it can oxidise S to SF_6 quite readily, *i.e.*, SF_6 is fromed quite easily.

Now in reaction (*b*), S is being reduced to SH_6 by H_2 which acts as a reducing agent. Since H_2 is a poor reducing agent, it cannot reduce S to SH_6, *i.e*. SH_6 will not be formed.

(*iii*) SF_6 is known but OF_6 is unknown.

Ans : The formation of OF_6 molecule requires the presence of six unpaired electrons in the valence-shell of O-atom. Due to the absence of *d*-orbitals in the valence-shell of O-atom, electrons from the completely-filled 2*s* and $2p_x$ orbitals ($O = 2s^2\ 2p^2_x\ 2p^1_y\ 2p^1_z$) cannot be promoted to get six unpaired electrons. Thus OF_6 molecule cannot be formed.

The formation of SF_6 molecule also requires six unpaired electrons. In this case, since S-atom has vacant 3*d* orbitals in its valence-shell, paired electrons present in 3*s* and $3p_x$ orbitals ($S = 3s^2\ 3p^2_x\ 3p^1_y\ 3p^1_z\ 3d^{\circ}$) can be promoted to the vacant 3*d* orbitals to get six unpaired electrons in the valence-shell. These six unpaired electrons can be used to form SF_6 molecule.

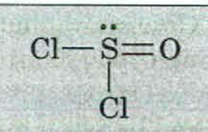
The whole discussion can be summarised by saying that OF_6 is not known due to the absence of *d*-orbitals in the valence-shell of O-atom while SF_6 is known because of the presence of *d*-orbitals (3*d*-orbitals) in the valence-shell of S-atom.

(*iv*) SF_6 is used as a gaseous electrical insulator.

Ans : SF_6 is a colourless, odourless and non-toxic gas at room temperature. It is thermally stable and chemically inert. Because of its interness and high tendency internal discharges, it is used as a gaseous electrical insulator in high voltage generators and switch gears.

(*v*) $SOCl_2$ can act as a weak acid as well as weak base.

Ans : The structure of $SOCl_2$ molecule is given in the margin. This structure shows that S-atom (central atom) has a *lp* of electrons on it. It is due to the presence of this *lp* of electrons that $SOCl_2$ acts as a base. Further, since S-atom has empty *d*-orbitals, it can accept electrons donoted by Lewis base, $SOCl_2$ also act as a Lewis acid.



Structure of $SOCl_2$ molecule

(*vi*) SF_6 is not easily hydrolysed though thermodynamically it should be but SF_4 can undergo hydrolysis.

Ans : In SF_6, S is sterically protected by six F atoms and hence does not allow H_2O molecules to attack the S-atom. Furthermore, F does not have *d*-orbitals to accept the electrons donated by H_2O molecules. As a result of these two reasons, SF_6 does not undergo hydrolysis. In contrast, in SF_4 S is not sterically protected, since it is surrounded by only four F atoms. As a result, attack of H_2O molecules can take place easily and hence hydrolysis occurs.

Q.2 Starting from elemental sulphur how would you prepare (*a*) SCl_2 and (*b*) SF_6 ?

Ans : Heating S and Cl_2 gives S_2Cl_2 which upon saturation with Cl_2 gives SCl_2. SF_6 is obtained by the direct combination of $S_8(g)$ and $F_2(g)$.

(*a*) $S_8(l) + 4Cl_2(g) \xrightarrow{\text{Heat}} 4S_2Cl_2(l)$

$S_2Cl_2(l) + Cl_2(g) \longrightarrow 2SCl_2(l)$

(*b*) $S_8(g) + 24F_2(g) \longrightarrow 8SF_6(g)$.

3. Among the hexafluorides SF_6, SeF_6 and TeF_6 which fluoride is not hydrolysed.

Ans : SF_6 is not hydrolysed.

University Questions

1. Write a note on the structure of oxides of sulphur. *(Delhi 86; GND 84; Meerut 86; Calcutta 86)*

2. Write a note on the structure of sulphurous acid molecule. *(Calcutta 86)*

3. Explain the structure of $H_2S_2O_4$ molecule.

4. How ii sod. hyposulphite ($Na_2S_2O_4$) prepared? What are its uses? *(Bharthiar 85, Madras 86)*

5. (*a*) Name the basic raw materials required for H_2SO_4 manufacture.

(*b*) How is dilute and concentrated H_2SO_4 stored?

(*c*) Why is 97% H_2SO_4 used for the absorption of SO_2 in contact process.

(*d*) How does SO_2 act as a food preservative? *(Delhi (I.C.) 87)*

6. Compare the structures of SO_3^{2-} and SO_4^{2-} ions. *(Delhi B.Sc. (Hons.) 85, 87)*

7. Write a note on "sodium thiosulphate". *(Jiwaji 84)*

8. Write a note on "Thionic acids". Give their structures. *(Utkal 86; Calicut 85; Andhra 85)*

9. Give an account of the preparation, properties, uses and structure of peroxyacids of sulphur. *(Allahabad 87, 89; Delhi 89; GND 84; Calcutta 86)*

10. Give methods of preparation, properties and uses of Marshall's perdisulphuric acid. *(Kanpur 2000)*

11. Give preparation, properties and applications of sodium thiosulphate. *(Lucknow 2000)*

12. Describe the preparation, properties and constitution of Care's acid and sodium thiosulphate. *(Avadh 2000)*

13. How does $Na_2S_2O_3.5H_2O$ react with I_2 solution and $AgNO_3$ solution? *(Bharahias 2000)*

14. Give the preparation, properties and uses of sodium thiosulphate. Give its structure. Why is it called hypo ? *(Meerut 2009)*

CHAPTER

37

General Characteristics of Group 17 (VII A) Elements : Halogens

Group VII A of the periodic table consists of five elements *viz. Fluorine* (F), *Chlorine* (Cl), *Bromine* (Br), *Iodine* (I) and *Astatine* (At). The elements F, Cl, Br and I are collectively called *Halogens.* The term *halogen* is derived from the Greek *halos* (= salt) and *genes* (= born) meaning salt producers because most of these elements exist in sea water, notably in the form of their sodium compounds. Astatine was discovered in 1940 and is an unstable element of radioactive origin. The other four elements are stable and resemble each other in physical and chemical properties.

Position of Halogens in the Periodic Table

The inclusion of halogens in the same sub-group VII A is justified by the following points :

I. Electronic Configurations.

The electronic configurations of the atoms of halogens are given as : F(Z = 9) → 2, 7 ($2s^2p^5$) ; Cl (Z = 17) → 2, 8, 7 ($3s^2p^5$); Br (Z = 35) → 2, 8, 18, 7 ($4s^2p^5$); I (Z = 53) → 2, 8, 18, 18, 7 ($5s^2p^5$); At (Z = 85) → 2, 8, 18, 32, 18, 7 ($6s^2p^5$). These configurations show that all the halogens have *seven* electrons (ns^2p^5) in their outer most shell. Two electrons are in *ns*-orbital and the remaining five electrons are in *np*-orbitals and are distributed as $np^2{}_x$, $np^2{}_y$, $np^1{}_z$ in accordance with Hunde's rule. The shell previous to the outermost shell contains in F the group s^2 (*saturated*), in Cl s^2p^6 (*saturated*), in Br $s^2p^6d^{10}$ (*saturated*) while in I and At $s^2p^6d^{10}$ (*unsaturated*). This shows why F differs from Cl and these two from the remaining elements. Since the additional electron in these elements enters the *p*-orbital of the outermost shell, these are called *p-block elements* of the long form of the periodic table.

II. Similarities in Physical Properties and Gradation in Them.

Some physical properties are discussed below :

1. Occurrence. These elements do not occur in the free state. But in the combined state they occur fairly abundantly in nature.

2. Diatomic Nature. Heat capacity and combining volume data have shown that all the halogens exist as covalent diatomic molecules (X_2 molecule) in the gaseous, liquid and crystalline states. These discrete X_2 molecules are held together by weak van der. Waals forces which explain the volatile nature of these elements. At high temperatures, X_2 molecules dissociate into X atoms. The stablility of diatomic molecules towards heat decreases from F_2 to I_2. No dissociation occurs in case of F_2 gas. Cl_2 is slightly dissociated above 1100°C, Br_2 about 6% while I_2 quite extensively above 1100°C.

3. Heat of Dissociation of X_2 Molecules. Heat of dissociation (ΔH_d) of X_2 molecule is the amount of heat required to dissociate X_2 molecule in the gaseous state into X gaseous atoms or to break X—X bond in X_2 molecule. Thus ΔH_d can be defined by the equation :

$$X_2\,(g) + \Delta H_d \longrightarrow 2\,X\,(g)$$

Obviously ΔH_d is equal to X—X bond energy. Excepting for F_2, ΔH_d values decrease from Cl_2 to I_2. The lower value of heat of dissociation of F_2 molecule as compared to Cl_2 molecule is due to the reasons namely : (*i*) Due to very small F—F bond length in F_2 molecule, repulsion between the non-bonding electrons is very large as compared to other X—X bond lengths (X = C1, Br, I). This makes the F atoms in F_2 molecule repel each other and helps the dissociation of F_2 molecule into F atoms. (*ii*) X—X bond in Cl_2, Br_2 and I_2 molecules is stronger than F—F bond in F_2 molecule. This is due to the possibility of the existence of multiple bonding in X—X bond involving *d*-orbitals.

4. Oxidising Property. A substance that has a tendency to accept one or more electrons is said to show oxidising property. The halogens, due to high electron affinity values, have a great tendency to accept an electron and hence act as strong oxidising agent. The oxidising property of a halogen molecule, X_2 is represented by :

$$\tfrac{1}{2}X_2\,(s,\,l \text{ or } g) + e^- + aq \longrightarrow X^-\,(aq) + \text{Energy released (E)}$$

The above reaction is accompanied by the release of energy (E) which is made up of many energy terms like heat of fusion, vaporisation etc. It has been seen that since the values of E are decreasing from F_2 to I_2, the oxidising power of halogens is also decreasing in the same direction, *i.e.* the oxidising power of halogens is in the order : F_2 (strongest oxidising agent) > Cl_2 > Br_2 > I_2 (weakest oxidising agent). Since F_2 is the strongest oxidising agent in the series, it will *oxidise* other halide ions to halogens in solution or when dry, *i.e.* F_2 displaces other halogens from their corresponding halides. For example :

$$\underset{(X^- = Cl^-,\,Br^-,\,I^-)}{F_2 + 2X^-} \longrightarrow 2F^- + X_2$$

Similarly Cl_2 will displace Br^- and I^- ions from their solutions and Br_2 will displace I^- ions from their solutions.

$$\underset{(X^- = Br^-,\,I^-)}{Cl_2 + 2X^-} \longrightarrow 2Cl^- + X_2$$

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

5. Heat of Hydration (ΔH_{hyd}) of X^- Ions. Heat of hydration of X^- ion (ΔH_{hyd}) is the amount of energy liberated in the process of converting $X^-(g)$ ion into hydrated $X^-(aq)$ ion.

$$X^-(g) + aq \longrightarrow X^-(aq) + \Delta H_{hyd}$$

Since ΔH_{hyd} represents the heat liberated, its value is shown by putting negative sign before it. It has been found that the value of ΔH_{hyd} becomes less negative as the size of X^- ion increases from F^- ion to I^- ion. It is because of the fact that the electrostatic interaction of a large X^- ion with water dipole becomes weaker than a smaller X^- ion and hence the magnitude of ΔH_{hyd} goes on decreasing.

6. Formation of Clathrates. Water solutions of the halogens on cooling give the crystals of their clathrates of $X_2. xH_2O$ type. Examples are : $Cl_2. 7.3\ H_2O$, $Br_2.10H_2O$, $I_2.xH_2O$ etc.

7. Eectronegativity. Halogens have large values of electronegativity. These values decrease as we proceed from F to I in the group. Large electronegativity values of halogen atoms indicate that X atoms have a strong tendency to form X^- ions.

8. Physical State and Density. There is a change of state from gas to solid and hence density increases as we move from F to I.

9. Atomic and Ionic Radii. These parameters increase as we descend the group form F to I.

10. Melting and Boiling Points. The melting and boiling points of the halogens regularly increase form F to I. This indicates that the attractive forces (van der Waals forces) between molecules become progressively more prominent as the molecules increase in size and mass. This effect is also reflected in the physical state of halogens. F and Cl are gases at ordinary temperatures, Br is a heavy liquid while I is a solid.

11. Colour. All the halogens are coloured. Their colour is due to the fact that their molecules absorb light in the visible region by means of which the outer electrons are excited to higher energy levels. The amount of energy required for the excitation (*i.e. excitation energy*) decreases progressively form fluorine to iodine as the size of the atom increases. Thus there is a progressive depeening of colour of the halogens from fluorine to iodine. Fluorine absorbs violet light (higher excitation energy) and hence appears *yellow*, while iodine vapour absorbs yellow light (lower energy) and appears *deep violet*. Similarly we can account for *greenish yellow* colour of chlorine and *reddish brown* colour of bromine.

12. Odour. All the halogens have very pungent and unpleasant odours. If inhaled even in very small quantities, they cause inflammation of the mucous membranes of the throat and nose and serious irritation of respiratory duets. Large quantities may have fatal effect.

13. Solubility. The halogens are slightly soluble in water and their solubility decreases from Cl to I. F cannot be dissolved in H_2O, since it decomposes H_2O liberating O_2 and some O_3. The halogens dissolve much better than H_2O in many organic solvents like carbon disulphide, chloroform, ether etc. Their higher solubility in organic solvents has been utilised to extract them from aqueous solutions. In organic solvents, iodine gives violet colour, bromine yields brown colour and chlorine produces yellow colour. It is assumed that in organic solvents halogens exist as free molecule as in the gas phase.

In nucleophilic (electron donating) polar solvent like alcohols, ketones, liquid SO_2, the halogens give coloured solutions whose colours are due to the formation of solvent $\rightarrow$ halogen type complexes. These complexes are charge-transfer compounds. In such compounds an electron located mainly in an orbital of the solvent molecule jumps into orbital located mainly on the halogen and absorbs energy from the light, causing the compound to look coloured. Such compounds have been isolated at low temperatures.

14. Ionisation Potentials. The ionisation potentials of halogens are very high which indicate that the halogens have a little tendency to lose an electron to form X^+ cation. These values progressively decrease from F to I, as the atomic size of these elements increases in the same order. With the decrease of ionisation potential from F to I, the tendency of these elements to lose an electron to form X^+ cation increase, *i.e.* F is not able to give F^+ cation while I forms I^+ cation easily. In other words, due to minimum value of ionisation potential of iodine, this elements shows *basic (non-metallic) character.*

15. Electron Affinity. Electron affinity values decrease from Cl to I. Why the electron affinity value of F is less than that of Cl has already been explained.

16. Oxidation States. Since these elements have ns^2p^5 configuration in their outermost shell, each halogen atom in its ground state can complete its octet either by accepting an electron from an element which is less electronegtive than it (*e.g.* alkali metals) to form a halide ion X^- or by sharing its unpaired electron in *p*-orbital with another element to form a covalent bond. When a halogen atom *in its ground state combines* with an element of lesser electronegativity than it, it shows –1 oxidation state. On the other hand when it combines with an element having greater electronegativity it exhibits +1 oxidation state. Since F is the most electronegative element, it always shows –1 oxidation state only. It does not exhibit any positive oxidation state. Cl, Br and I have vacant *d*-orbitals in their valence-shell and, therefore, can have excited states (*i.e.* CI, Br and I can promote their *s*-and *p*-electrons to the vacant *d*-orbitals), which make it possible for these elements to exhibit higher positive oxidation states of + 3, + 5 and + 7. Higher oxidation states of I equal to + 3, + 5 and + 7 have already been explained.

Since F atom has no *d*-orbital in its valence-shell, it cannot have any excited state and consequently cannot exhibit any of the higher oxidation states. In case of bromine the penultimate shell *viz.* $3s^2p^6d^{10}$ is weakly screened and hence the energy required to promote an electron from 4*s*-orbital of the atom in the second excited state to 4*d*-orbital is markedly higher than that required in chlorine. Thus Br does not exhibit + 7 oxidation state.

Since all the halogens, excepting fluorine, are less electronegative than oxygen, they show positive oxidition states in their oxygen compounds *viz.* oxides and oxy acids, *e.g.*, Cl in ClO_2 and Br in BrO_3 show + 4 and + 6 oxidation states and similary Cl in HClO, $HClO_2$, $HClO_3$ and $HClO_4$ show + 1, + 3, + 5 and + 7 oxidation states respectively. In interhalogen compounds the halogen with lower electronegativity (having higher atomic number or atomic radius) shows positive oxidation state, *e.g.* I in ICl and Cl in ClF show + 1 oxidation state each. Note that Cl in ICl shows –1 oxidation, state while in ClF it shows + 1 oxidation state.

III. Similarities in Chemical Properties and Gradation in Them.

Some chemical properties are discussed below :

1. Reactivity. All the halogens are the most reactive elements as a family. The main reasons for their extreme reactivity are : (*a*) Dissociation energies in (KJ/mole) of X_2 molecules and other diatomic molecules like N_2, O_2 and H_2 are : $N_2 = 941.62$, $O_2 = 495.08$, $H_2 = 431.89$, $F_2 = 157.77$, $Cl_2 = 237.38$, $Br_2 = 189.99$, $I_2 = 148.56$. These values show that X_2 molecules have *low values* and hence it is much easier for these molecules to dissociate into X atoms and react with other substances more readily as compared to other diatomic molecules like N_2, O_2 and H_2. (*b*) Because of *high electron affinity values* of halogen atoms, halogens have a strong tendency to add on electron to form X^- ion.

The reactivity of halogen atoms decreases as we move down the group from F to I. For example fluorine decomposes H_2O vigorously even in dark, chlorine decomposes H_2O in sunlight, bromine also decomposes H_2O in sunlight but very slowly while iodine does not decompose water at all.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2;\ Cl_2 + H_2O \longrightarrow HClO + HCl$$

$$Br_2 + H_2O \longrightarrow HBrO + HBr;\ I_2 + H_2O \longrightarrow \text{No reaction}$$

2. Formation of Hydracids. All the elements of this group combine with hydrogen and form hydrogen halides (HX) which are called hydracids or halogen acids. The affinity of these elements for hydrogen decreases from fluorine to iodine. Thus F_2 combines with H_2 explosively and even in the dark, Cl_2 reacts with H_2 in diffused sunlight, Br_2 reacts with H_2 only on heating above 500°C while I_2 reacts with H_2 only on heating and in presence of Pt as a catalyst. This clearly shows that the tendency of the halogens to react with H_2 decreases from F_2 to I_2. The reaction of I_2 with H_2 is reversible and endothermic. Hydracids can be prepared by the direct combination of the elements, by heating the metal halides with conc. H_2SO_4, by the hydrolysis of non-metallic halides etc. Some important properties of hydracids are given below :

(i) Acidic properties. All the halogen acids in the gaseous state are essentially covalent but in the aqueous solution they ionise to give the solvated proton (H_3O^+) and hence act as acids.

$$H_2O + HX \longrightarrow H_3O^+ + X^-$$

HF ionises only slightly while HCl, HBr and HI ionise completely. Hence HF is the weakest acid and the strength of these acids increases from HF to HI, *i.e.* HF (weakest acid) < HCl < HBr < HI (strongest acid). The weakest acidic nature of HF is due to the fact that the dissociation energy of H—F bond in HF molecule is the highest (= 564.97 $KJ.mol^{-1}$) and hence this molecule has least tendency to split up into H^+ and F^- ions in aqueous solution. Another explanation of the above order of the acidic strength of HX acids can be given by finding out the relative order of the basicity of the conjugate bases *viz.* F^-, Cl^-, Br^- and I^- of these acids. This explanation has already been given. The hydrides show no acidic character when perfectly dry.

(ii) Covalent character. The bond between hydrogen and the halogen in these hydrides is *largely covalent* as is indicated by their low melting and boiling points and also by the fact that the pure liquid hydrogen halides are poor conductors of electricity. The bonds do, however, have small amount of polar character which decreases with the decrease of electronegativity of the halogen atom. Thus the polar character of H—X bond in HX molecules decreases in the order : H—F > H—Cl > H—Br > H—I.

(iii) Physical properties. Anhydrous HF is a liquid at ordinary temperature whereas other HX (X = Cl, Br, I) are colourless gases. These have sharp choking odour. Excepting HF, the melting and boiling points of these hydrides increase with the increase of the atomic weight of the halogen atom. The abnormally high melting point of HF is explained by saying that, due to H-bonding, HF molecule gets associated to form $(HF)_6$ which is an aggrevated molecule.

The values of heat of formation increase with the increase of atomic weight of halogen atom. Thus the quantity of energy released during the formation of HX molecules decreases from HF to HI.

(iv) Stability and reducing property. As we go from HF to HI, the stability of these acids decreases from HF to HI. (HF > HCl > HBr > HI). Thus HF and HCl are stable upto 1200°C while HBr dissociates slightly (1%) and HI dissociates at 440°C to 20%.

The decrease in the stability of HX molecules from HF to HI implies that the reducing properties of these acids increase from HF to HI, *i.e.* HF < HCl < HBr < HI.

The above order shows that HF has no appreciable reducing properties while HI is the strongest reducing agent. Even dilute solution of HI, on exposure to the air, slowly acquires a brown colour due to the liberation of I_2.

$$4HI + O_2 \ (\textit{From atmosphere}) \longrightarrow 2H_2O + 2I_2$$

3. Formation of Binary Halogen-oxygen Compounds. Halogens do not combine directly with O_2. However, binary halogen-oxygen compounds can be prepared by indirect methods. Examples of such compounds are : OF_2, O_2F_2, Cl_2O, ClO_2, Br_2O, BrO_2, I_2O_4, I_2O_5 etc. F being more electronegative than oxygen, OF_2 and O_2F_2 are called fluorides of oxygen and not oxides of fluorine.

4. Formation of Oxy-acids. Excepting F, all other halogens form oxy-acids. These are mainly of four types *viz.* HXO (*e.g.* HClO, HBrO, HIO); HXO_2 (*e.g.* $HClO_2$); HXO_3 (*e.g.* $HClO_3$, $HBrO_3$, HIO_3) and HXO_4 (*e.g.* $HClO_4$, $HBrO_4$, HIO_4). Some of their properties are given below :

(i) Acidic character. (*a*) In the series of oxy-acids of the same halogen in different oxidation number the acidic character of such acids increases with the increase of the oxidation number of the halogen. Thus the acidic character of HClO, $HClO_2$, $HClO_3$, $HClO_4$ acids is in the order. HClO (+ 1) < $HClO_2$(+ 3) $HClO_3$(+ 5) < $HClO_4$(+ 7). Oxidation number of Cl atom in each acid is given in parentheses.

Explanation. The above order of acidic character of the acids is explained by finding out the relative order of the basicity of the conjugate bases (*viz.* ClO^-, ClO_2^-, ClO_3^- and ClO_4^-) of these acids. This has already been explained.

(*b*) The acidic character of the oxy-acids of different halogens in the same oxidation state decreases, in general, with decrease of the electronegativity of the halogen atom. Thus the acidic character of HClO, HBrO and HIO acids is in the order : HClO(Cl = 3.0) > HBrO (Br = 2.8) > HIO(I = 2.5). The electronegativity of halogen atoms is given in bracket.

Explanation. As the atomic number of the halogen atom increases, its electronegativity decreases and size increases; As a result of this, the tendency of these acids to lose a proton to water decreases. This makes the acid a weaker acid.

(ii) Oxidising power. As the oxidation number of the halogen atom increases, X—O bond becomes more covalent, resulting in a decrease of the oxidising power of the acid. For example under usual laboratory conditions, the oxidising action of HClO, $HClO_2$, $HClO_3$, and $HClO_4$ acids is in the order HClO(+ 1) > $HClO_2$(+ 3) > $HClO_3$(+ 5) > $HClO_4$(+ 7). In brackets are given the oxidation number of chlorine atom in the respective acid.

(iii) Thermal stabitity. With the increase of oxidation number of the halogen atom, X—O bond in the oxy-acids becomes more covalent and hence thermal stability of the acids increases. Thus the thermal stability of HClO, $HClO_2$, $HClO_3$ and $HClO_4$ acids is in the order : HClO(+ 1) < $HClO_2$(+ 3) < $HClO_3$(+ 5) < $HClO_4$(+ 7).

In the series of oxy-acids of different halogens in the same oxidation state, thermal stability of these acids decreases, in genera], with the decrease of the electronegativity of the halogen atom. For example thermal stability of HXO acids (X = Cl, Br, I) is in the order : HClO(Cl = 3.0) > HBrO(Br = 2.8) > HIO(I = 2.5)

5. Formation of Interhalogen Compounds. Two different halogen atoms, due to the difference in their electronegativity values, combine with one another to form a number of covalent compounds which are called interhalogen compounds. These are of four types namely AB (*e.g.* ClF, BrF etc); AB_3 (*e.g.* ClF_3, BrF_3, ICl_3); AB_5(*e.g.* BrF_5, IF_5) and AB_7 (*e.g.* IF_7) where A and B are two different halogen atoms.

6. Formation of Polyhalides. In some cases halogens combine with simple metallic halides (*e.g.* KI, KBr, CsCl) and form polyhalides like $K^+[I_3]^-$, $K^+[Br_3]^-$, $Cs^+[ClF_4]^-$ etc.

Anomalous Behaviour of Fluorine : Dissimilarities of Fluorine with Other Halogens.

Like other elements such as C, N and O which are the first members of their respective groups, fluorine also differs from the other members of its own sub-group due to (*a*) *its small size* (*b*) *its high electronegativity and* (*c*) *non-availability of d-orbitals in its valence shell. The main differences* are : (*i*) Due to its maximum electronegativity, *it shows only a negative oxidation state of –1. It does not show any positive oxidation state.* The other members show negative as well as positive oxidation states of + 1, + 3, + 5 and + 7. (*ii*) Fluorine is the most reactive element among halogens. This is due to the minimum value of F—F bond dissociation energy. (*iii*) On account of high electronegativity of fluorine atom hydrogen bonding occurs in HF molecule while it is absent in HCl, HBr and HI molecules. The presence of hydrogen bonding in HF explains why (*a*) HCl, HBr and HI are gaseous while HF is a liquid with an abnormally high boiling point (*b*) HF forms a number of compounds containing HF_2^- ion (*e.g.* $K^+HF_2^-$) while such compounds (*e.g.* $K^+HCl_2^-$, $K^+HBr_2^-$ etc.) are not given by other HX molecules. (*iv*) HF ionises only slightly in aqueous solution and is, therefore a weak acid. HCl, HBr and HI, on the other hand, ionise almost completely and are thus strong acids. (*v*) Fluoride of silver is soluble while other halides of silver are insoluble. Similarly fluoride of calcium is insoluble and other halides of calcium are soluble. (*vi*) Fluorides are ionic while other halides have frequently *molecular lattices.* (*vii*) F ion has a great tendency to give complex ions like $[AlF_6]^{3-}$, $[FeF_6]^{3-}$ etc. The remaining halide ions show this tendency to a much lesser extent. (*viii*) Fluorine, being the most electronegative, gives SF_6 while other members do not form hexahalides with sulphur. (*ix*) Because of the absence of *d*-orbitals in its valence shell, fluorine does not combine with F ions to give polyhalide ion, F_3^- while other members of the group give such ions (*e.g.* Cl_3^-, Br_3^-, I_3^-, I_5^- etc.) because they contain *d*-orbitals.

Comparison of Fluorine and Oxygen.

Fluorine resembles oxygen which is the first member of the neighbouring group *viz.* VIA in some respects on account of the following factors : (*a*) *The atomic and ionic radii of both the elements are very similar (b) Both are highly electronegative.*

(A) Similarities. (*i*) Both of them exist in gaseous state at ordinary temperature (*ii*) Both react with metals (*e.g.* Na) and non- metals (*e.g.*, H, C, Si, S etc.) to give fluorides and oxides which resemble each other in solubilty, volatility, fusibility etc., *e.g.* HF and H_2O resemble each other in the following respects (*a*) Both possess associated molecules, $(H_2O)_x$ and $(HF)_x$ respectively due to hydrogen bonding (*b*) The boiling points of both are abnormally high (*c*) HF like H_2O is a weak acid and both are ionising solvents. (*d*) Heats of formation of HF and H_2O are close to each other. (*iii*) Certain elements like sulphur exhibit higher valencies in both fluorides and oxides, *e.g.* the valency of sulphur in SF_6 and SO_3 is 6.

(B) Dissimilarities. However these elements differ from each other in the following respects : (*i*) F is always monovalent while oxygen is bivalent (*ii*) F is more reactive than oxygen.

Basic Properties of Halogens

In general, the metallic (*i.e.* basic) character of the elements increases on descending a group while the same decreases on proceeding from left to right in a period. Thus the halogens should be expected to show the minimum basic character and among halogens themselves astatine (the last member of the halogen family) should be the most basic in character. Unfortunately no evidence is available which may prove the basic character of astatine. Iodine which is the next heaviest halogen shows maximum basic properties in halogen family elements. Note that *iodine is not a metal.* A progressive increase in the basic character from F to I is due to the factors *viz.* (*i*) Electronegativity *decreases* from F to I (*ii*) Electron affinity *decreases* from Cl to I (*iii*) Ionisation potential *decreases* from F to I.

Flourine is the most electronegative element and as such it does not show any basic character at all, *i.e.* it has no tendency to form positive ions in any of its known compounds. The nonexistence of the oxy-acids of F further confirms our belief that F is unable to bear a positive charge. There is, however, evidence for the existence of basic properties in Cl, Br and I. Chlorine has a slight tendency to form positive ions, *e.g.* Cl shows + 1 oxidation state in OCl^-, Cl_2O, ClF etc. species and exhibits + 3 oxidation state in ClO^-_2, ClF_3 etc. species, since O and F are more electronegative than Cl (O = 3.5, F = 4.0 and Cl = 3.0). Bromine exists as Br^+ in Br_2O and BrF (Br = 2.8) and as Br^{3+} in complexes containing $[BrF_2]^+$ ion such as $[BrF_2]^+ [Sb^{5+}F_6]^-$, $[BrF_2]^+ [Sn^{4+}F_6]^{2-}$. The compounds in which iodine functions as cationic (*i.e.* positive) constituent are numerous and well established. Some of the compounds containing *unipositive iodine*, I^+ are ICl, IBr, INO_3, I_2SO_4, $[Ipy_2]^+X^-$ ($X = NO_3^-$, ClO_4^-). $I(ClO_4)_3$, $I(CH_3COO)_3$, IPO_4, $I(NO_3)_3$, ICl_3 etc. are some compounds presumably containing *tripositive* iodine, I^{3+}. I_2O_4 or $[I^{3+}O]^+[I^{5+}O_3]^-$ which is called iodyl iodate contains both I^{3+} and I^{5+} cations.

Compounds Containing Cationic Iodine

Following are the important compounds containing unipositive iodine (I^+) or tripositive iodine (I^{3+}).

1. ICl and IBr interhalogen compounds. For the preparation and properties of these compounds see chapter 41.

2. Iodine nitrate (INO_3) and iodine sulphate (I_2SO_4). Solutions of these compounds are obtained by passing a solution of H_2SO_4 and of HNO_3 respectively in absolute alcohol through exchanger containing sorbed I^+ ion.

$$2I^+R^- + H_2SO_4 \longrightarrow I_2SO_4 + 2HR$$
$$I^+R^- + HNO_3 \longrightarrow INO_3 + HR$$

When the aqueous solutions of these compounds are electrolysed, iodine is liberated at cathode, proving that both of these salts contain unipositive iodine, I^+.

3. Complex compounds of $[Ipy_2]^+X^-$ type ($X = NO_3^-$, ClO_4^-). In these compounds I^+ ion gets stabilised by coordination. These compounds are obtained by treating Ag(I) salt with I_2 in chloroform in presence of excess of pyridine (py). For example :

$$AgNO_3 + I_2 + 2py \longrightarrow \underset{\text{ppt.}}{AgI} + [Ipy_2]NO_3$$

Complexes of this type have the following properties. We shall consider $[Ipy_2]NO_3$ as an example.

(*i*) *Reaction with acidified KI solution.* When $[Ipy_2]NO_3$ reacts with acidified KI solution, I_2 is liberated.

I^+ (From complex compound) + I^- (From KI) $\longrightarrow I_2$

I_2 liberated in the above reaction can be quantitatively estimated with sod. thiosulphate.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

(*ii*) *Electrolysis.* Electrolysis of $[Ipy_2]NO_3$ in chloroform liberates iodine at the cathode.

$2I^-$ (From the complex compound) + $2e^- \longrightarrow I_2$ (*At cathode*)

These reactions show the presence of I^+ ion in the complex compound.

(*iii*) *Hydrolysis.* The complex compound is hydrolysed by water as follow :

$$5[Ipy_2]NO_3 + 3H_2O \longrightarrow 5HNO_3 + 10py + HIO_3 + 2I_2$$

(*iv*) *Reaction with NaOH.* Treatment of the complex compound with NaOH gives the base, $[Ipy_2]OH$ which is converted into its anhydride.

$$[Ipy_2]NO_3 + NaOH \longrightarrow \underset{\text{Base}}{[Ipy_2]^+(OH)^-} + NaNO_3$$

$$\underset{\text{Base}}{2[Ipy_2]OH} \longrightarrow \underset{\substack{\text{Anhydride of} \\ \text{the base}}}{Ipy\text{—}O\text{—}Ipy} + H_2O + 2py$$

(*v*) *Reaction with phenol (C_6H_5OH) gives tri-iodophenol.*

$$C_6H_5OH + 3[Ipy_2]NO_3 \longrightarrow \underset{\text{Tri-iodophenol}}{C_6H_2I_3OH} + 3HNO_3 + 6py$$

(*vi*) *Noble metals like Au get dissolved in chloroform solution of the complex compound.*

$$3[Ipy_2]NO_3 + Au \longrightarrow Au^{3+} + 3NO_3^- + \tfrac{1}{2}I_2 + 6py$$

In $[Ipy_2]$ NO_3 and other similar compounds I^+ appears to be two-coordinate and hence the complex, $[Ipy_2]^+NO_3^-$ should be formulated as $[pyIpy]^+NO_3^-$.

4. Iodine perchlorate, $I(ClO_4)_3.2H_2O$. It is formed as yellowish-green needles by the action of O_3 on a cooled solution of I_2 in anhydrous $HClO_4$.

$$I_2 + 6HClO_4 + O_3 \longrightarrow 2I(ClO_4)_3 + 3H_2O$$

When the aqeous solution of this compound is electrolysed, iodine is liberated at cathode.

$$I(ClO_4)_3 \longrightarrow I^{3+} + 3ClO_4^-$$
$$2I^{3+} + 6e^- \longrightarrow I_2 \text{ (At cathode)}$$

5. Iodine triacetate, $I(CH_3COO)_3$. It is obtained by oxidising I_2 in acetic anhydride, $(CH_3.CO)_2O$ with fuming HNO_3.

It is a crystalline colourless substance, stable in cold but decomposes at 100°C. The saturated solution of the compound in acetic anhydride conducts electricity and during electrolysis I is liberated at the cathode (of silver), forming AgI.

$$(CH_3COO)_3\ I \rightleftharpoons I^{3+} + 3CH_3COO^-$$
$$I^{3+} + 3e^- + Ag \longrightarrow AgI \text{ (At silver cathode)}$$

6. Iodine trichloride, ICl_3. For the preparation, properties and uses of this compound see chapter 47.

Conceptual Questions with Answers

Q.1 Fluorine does not undergo disproportionation reactions but other halogens do. Explain.

Ans : F-atom shows only – 1 oxidation state. When this atom undergoes disproportionation reaction, its O.S. should be decreased from – 1 to some lower O.S. (reduction) and also should be increased from – 1 to some higher O.S. (oxidation). None of these processes is possible, since F-atom does not show any O.S. other than – 1. On the other hand, since other halogens show – 1, + 1,

+ 3, + 5 and + 7 oxidation states, the oxidation and reduction of these halogens both are possible. Hence other halogens can undergo disproportionation reactions.

Q.2 Explain the following, giving appropriate reasons for your answer.

(*i*) HF and HCl can be prepared by the action of conc. H_2SO_4 on CaF_2 and NaCl respectively but HBr and HI cannot be prepared by the action of conc. H_2SO_4 on NaBr and NaI (or KI) respectively.

Ans : When CaF_2 and NaCl are heated separately with conc. H_2SO_4, HF and HCl are produced.

$$\mathrm{CaF_2 + H_2SO_4 \xrightarrow{\Delta} CaSO_4 + \boxed{2HF}}$$

$$\mathrm{2NaCl + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + \boxed{2HCl}}$$

When NaBr and NaI are heated with conc. H_2SO_4, HBr and HI are first formed which, being moderate reducing agents (RA), reduce H_2SO_4 to SO_2 and are themselves oxidised to Br_2 and I_2 respectively.

$$\begin{array}{lllllllll}
\mathrm{2NaBr} & + & \mathrm{H_2SO_4} & \xrightarrow{\Delta} & \mathrm{Na_2SO_4 + 2HBr} & & & & \\
\mathrm{2HBr} & + & \mathrm{H_2SO_4} & \longrightarrow & \mathrm{SO_2} & + & \mathrm{2H_2O} & + & \mathrm{Br_2} \\
(\mathrm{Br} = -1) & & (\mathrm{S} = +6) & & (\mathrm{S} = +4) & & & & (\mathrm{Br} = 0) \\
(\mathrm{RA}) & & (\mathrm{OA}) & & & & & & \\
\hline
\mathrm{2NaBr} & + & \mathrm{2H_2SO_4} & \longrightarrow & \mathrm{Na_2SO_4 + SO_2 + 2H_2O} & + & \boxed{\mathrm{Br_2}} & &
\end{array}$$

or

$$\begin{array}{lllllllllll}
\mathrm{2Br^-} & + & \mathrm{SO_4^{2-}} & + & \mathrm{4H^+} & \longrightarrow & \mathrm{SO_2} & + & \mathrm{2H_2O} & + & \mathrm{Br_2} \\
(\mathrm{Br} = -1) & & (\mathrm{S} = +6) & & & & (\mathrm{S} = +4) & & & & (\mathrm{Br} = 0) \\
(\mathrm{RA}) & & & & & & & & & &
\end{array}$$

Similary,

$$\begin{array}{lllllllll}
\mathrm{2NaI}\ (or\ \mathrm{2KI}) & + & \mathrm{H_2SO_4} & \xrightarrow{\Delta} & \mathrm{Na_2SO_4 + 2HI} & & & & \\
\mathrm{2HI} & + & \mathrm{H_2SO_4} & \longrightarrow & \mathrm{SO_2} & + & \mathrm{2H_2O} & + & \mathrm{I_2} \\
(\mathrm{I} = -1) & & (\mathrm{S} = +6) & & (\mathrm{S} = +4) & & & & (\mathrm{I} = 0) \\
(\mathrm{RA}) & & (\mathrm{OA}) & & & & & & \\
\hline
\mathrm{2NaI} & + & \mathrm{2H_2SO_4} & \longrightarrow & \mathrm{Na_2SO_4 + SO_2 + 2H_2O} & + & \boxed{\mathrm{I_2}} & &
\end{array}$$

or

$$\begin{array}{lllllllllll}
\mathrm{2I^-} & + & \mathrm{SO_4^{2-}} & + & \mathrm{4H^+} & \longrightarrow & \mathrm{SO_2} & + & \mathrm{2H_2O} & + & \mathrm{I_2} \\
(\mathrm{I} = -1) & & (\mathrm{S} = +6) & & & & (\mathrm{S} = +4) & & & & (\mathrm{I} = 0) \\
(\mathrm{RA}) & & & & & & & & & &
\end{array}$$

(*ii*) In the preparation of HBr and HI from NaBr and KI respectively, phosphoric acid (H_3PO_4) is preferred to H_2SO_4.

Ans : When NaBr and NaI are heated with conc. H_2SO_4, HBr and HI are produced.

$$\mathrm{2NaBr + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2HBr}$$

$$\mathrm{2NaI + H_2SO_4 \xrightarrow{\Delta} K_2SO_4 + 2HI}$$

Now since H_2SO_4 is an OA and HBr/HI is RA, H_2SO_4 oxidises HBr and HI to Br_2 and I_2 respectively.

$$\underset{\text{OA}}{H_2SO_4} + \underset{\text{RA}}{2HBr} \longrightarrow SO_2 + 2H_2O + Br_2$$

$$\underset{\text{OA}}{H_2SO_4} + \underset{\text{RA}}{2HI} \longrightarrow SO_2 + 2H_2O + I_2$$

If we use H_3PO_4 in place of H_2SO_4, this acid also gives HBr and HI but, since this acid is non-oxidising, this acid does not oxidise HBr and HI as H_2SO_4 does.

$$3NaBr + H_3PO_4 \longrightarrow Na_3PO_4 + 3HBr$$
$$3KI + H_3PO_4 \longrightarrow K_3PO_4 + 3HI$$
$$HBr + H_3PO_4 \longrightarrow \text{No reaction}$$
$$HI + H_3PO_4 \longrightarrow \text{No reaction}$$

***(iii)* Among the tetrahalides of lead, only PbF_4 and $PbCl_4$ are quite stable while $PbBr_4$ and PbI_4 are unstable (unknown or donot exist).**

Ans : We know that the halide ions are reducing agents and their reducing power is in the order : $F^- < Cl^- < Br^- < I^-$.

On ionisation, PbI_4 gives Pb^{4+} and I^- ions. Now since I^- ion is a very strong RA, this ion reduces Pb^{4+} to Pb^{2+} and is itself oxidised to I_2.

$$PbI_4 \longrightarrow Pb^{4+} + 4I^-$$
$$Pb^{4+} + \underset{\text{(RA)}}{2I^-} \longrightarrow Pb^{2+} + I_2$$

$$PbI_4 \longrightarrow \underbrace{Pb^{2+} + 2I^-} + I_2$$

or $$\underset{\text{(unstable)}}{PbI_4} \longrightarrow PbI_2 + I_2$$

Thus we see that PbI_4 is reduced to PbI_2 and hence is unstable.

Similary, since Br^- ion is also a strong RA, Pb^{4+} ion gets reduced to Pb^{2+} and Br^- ion oxidised to Br_2.

$$PbBr_4 \longrightarrow Pb^{4+} + 4Br^-$$
$$Pb^{4+} + \underset{\text{(RA)}}{2Br^-} \longrightarrow Pb^{2+} + Br_2$$

$$PbBr_4 \longrightarrow Pb^{2+} + 2Br^- + Br_2$$

or $$\underset{\text{(unstable)}}{PbBr_4} \longrightarrow PbBr_2 + Br_2$$

Thus $PbBr_4$ is also unstable.

On ionisation, PbF_4 and $PbCl_4$ both give Pb^{4+} and X^- ions ($X^- = F^-, Cl^-$). Now since these halide ions are very weak reducing agents, these ions are not able to reduce Pb^{4+} ions to Pb^{2+} ions and hence PbX_2 is not formed.

$PbX_4 \longrightarrow Pb^{4+} + 4X^-$ ($X^- = F^-, Cl^-$)

$Pb^{4+} + 2X^- \longrightarrow Pb^{2+} + X_2$ (*This reaction does not take place*)

Thus PbF_4 and $PbCl_4$ are stable compounds.

Q.3 KHF_2 is well known while $KHCl_2$, $KHBr_2$ and KHI_2 donot exist. Explain with reasons.

Ans : The answer of this question can be given in the following two ways.

(*a*) KHF_2 can be regarded as having been obtained by the combination of KF and HF.

$$KF + HF \longrightarrow K^+[HF_2]^-$$

As a matter of fact the formation of $K^+[HF_2]^-$ takes place through the following two steps :

$$KF \longrightarrow K^+ + F^- \quad ...(i)$$

$$F^- + H - F \longrightarrow [F...H{-}F]^- \text{ or } [HF_2]^- \quad ...(ii)$$

On adding : $KF + HF \longrightarrow K^+[F...H{-}F]^- \text{ or } K^+[HF_2]^-$

Because of high electronegativity of F^- ion, the combination of this ion with HF molecule to form $[HF_2]^-$ ion as shown at step (*ii*) takes place through H-bonding. Since the electronegativity values of Cl^-, Br^- and I^- are comparatively smaller, these ions cannot combine with HCl, HBr and HI molecules through H-bonding and hence $[HCl_2]^-$, $[HBr_2]^-$ and $[HI_2]^-$ ions are not formed. In other words we can say that following reactions are not feasable.

$$\left.\begin{array}{l} KCl + HCl \longrightarrow K^+[HCl_2]^- \\ KBr + HBr \longrightarrow K^+[HBr_2]^- \\ KI + HI \longrightarrow K^+[HI_2]^- \end{array}\right\} \textit{These reactions donot take place.}$$

(*b*) We know that hydrofluoric acid exists as a dimeric molecule (H_2F_2) due to H-bonding. Thus this acid is a dibasic acid and hence ionises in the following two ways :

$$H_2F_2 \longrightarrow H^+ + HF_2^-$$

$$HF_2^- \longrightarrow H^+ + 2F^-$$

Obviously H_2F_2 can form two types of salts like $K^+[HF_2]^-$ or $K^+[F...H{-}F]^-$ and K^+F^-. Because of the absence of H-bonding in HCl, HBr and HI molecules, these acids exists as monomeric molecules. Consequently these acids give only one type of salts like KCl, KBr and KI.

University Questions

1. Discuss the position of the elements of group VIIA in the periodic table. (*Agra 84*)
2. Compare the methods of preparation and properties of various halogen acids. (*Meerut 86*)
3. Arrange the hydrides of halogens with reasons, in the increasing order of heat of vaporisation, bond energy, ionic character dipole moment, reducing power, strength, heat of formation, acidic character, thermal stability and bond length. (*R.E.E. 84*)
4. How does fluorine differ from other halogens. (*Avadh 2000*)
5. Discuss the abnormal behaviour of fluorine. (*Meerut 2009*)

CHAPTER

38

Fluorine and Fluorocarbons

Fluorine

History of its Isolation

It was known to *Schwankhard* (1670) that glass is attacked when exposed to the fumes obtained by heating fluorspar with conc. H_2SO_4. In 1771 *Scheele* heated fluorspar with conc. H_2SO_4 in a tin retort and obtained an acid solution. By his experiment he concluded that fluorspar is the calcium salt of this acid solution which he named *fittoric acid. Gay Lasac and Thenard* in 1809 prepared this acid and showed that the acid resembles hydrochloric acid in many properties and on analogy they named it *hydrofluoric acid.* In 1813 *Day* showed that hydrofluoric acid was a compound of H_2 and an unknown element which he named *fluorine.* Davy tried to prepare fluorine by the electrolysis of aqueous solution of hydrofluoric acid just as Cl_2 is obtained of the electrolysis of aqueous solution of HCl. To his great surpr1se he obtained H_2 and ozone mixed with O_2, instead of fluorine, at the anode. For being most resistant to oxidation, H_2O gets oxidised at the anode liberating O_3 mixed with O_2.

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$$
$$3H_2O \longrightarrow 6H^+ + O_3 + 6e^-$$

Gore then attempted to electrolyse the anhydrous hydrofluoric acid to isolate fluorine from it, but he found this acid to be non-conductor and hence failed to isolate fluorine from it. In 1860 he showed that the anhydrous acid dissolves in KHF_2 and gives a conducting solution. But another problem was that of great chemical reactivity of fluorine. It attacked the apparatus whether made of glass, carbon and platinum. When platinum vessel was used, it gave a chocolate powder of PtF_4 while with carbon it gave the gaseous CF_4. It was in 1886 that the long standing problem was finally solved by *Moisson.* He prepared fluorine by electrolysing a solution of KHF_2 (1 part) in anhydrous hydrofluoric acid (5 parts) in a U-tube made of Pt—Ir alloy using electrodes of the same alloy. He reduced the great chemical reactivity of fluorine by keeping the bath and collecting the gas at very low temperature.

What Were the Difficulties Encountered in the Discovery and Isolation of Fluorine?

For a long time a number of difficulties were experienced in the discovery and isolation of fluorine. The main difficulties (or causes) for the late discovery and isolation of fluorine are (*i*) *Extreme reactivity of fluorine.* Fluorine is so reactive that it reacts with the material of all the vessels, *e.g.* F_2 attacks carbon and silicon present in the glass vessels with the formation of CF_4 and SiF_4

respectively. . Similarly F_2 also attacks the electrodes and vessels made of Pt with the formation of chocolate coloured powder, PtF_4. Pb, Fe and Sn vessels were also tried and found to be unsuitable for the preparation of fluorine. Thus no metal could be employed for the preparation of F_2 as vessel or as electrode. (*ii*) *Greater stability and non-conducting nature of hydrofluoric acid.* Hydrofluoric acid is very stable, highly poisonous and corrosive in nature. It is so stable that all attemps to isolate F_2 from hydrofluoric acid by oxidising agents failed. Moreover, electrolysis of aqueous solution of hydrofluoric acid gives H_2 and ozone mixed O_2 while anhydrous hydrofluoric acid is non-conductor.

Occurrence

Fluorine is very reactive and hence does not occur free in nature but is widely found in the combined state as fluorides. Its chief minerals are : *fluorspar*, CaF_2; *cryolite*, Na_3AlF_6 and *fluoraptite*, $CaF_2.3Ca_3(PO_4)_2$. Small quantities of fluorine are present as fluoride in plant-ash, soil, sea-water, river water plants, bones and teeth of animals. One litre of sea-water contains about 2 mg. of fluorine. Fluorine is also found in the phosphate *rocks*. *Fluorspar*, CaF_2 is the principal source of fluorine and its compounds. A six mile long belt of fluorspar has been recently discovered in Durgapur (Rajasthan) and it is considered to be sufficient to meet the need of the country.

Isolation

Different methods employed for the isolation of F_2 are given below :

1. Moissan's Method. (*Historical method—1886*). This is a historical method, since this method was used for the first time by Moissan to isolate fluorine. Essential parts of the electrolytic cell used by Moissan are : (*a*) *Electrolytic cell.* Electrolytic cell consists of a U-shaped tube made of Pt—Ir alloy cooled at –23°C by placing it in a bath of CH_3Cl (b.pt. = –23°C) which was constantly renewed. (*b*) *Electrodes.* These are made of Pt—Ir alloy and are insulated with fluorspar stoppers covered with shellac. (*c*) *Electrolyte.* Electrolyte consists of a solution of *potassium hydrogen fluoride*, KHF_2 (1 part) in anhydrous hydrofluoric acid, H_2F_2 (5 parts).

Process. Moissan took the solution consisting of KHF_2 and anhydrous H_2F_2 (in 1 : 5 ratio) in a U-shaped electrolytic cell at a temperature of –23°C by placing the cell in a bath of CH_3Cl and electrolysed this solution (Fig. 38.1). On electrolysis H_2 was liberated at the cathode and F_2 at the anode which is passed through platinum spiral tube similarly placed in the bath of methyl chloride (CH_3Cl). The vapours of hydrofluoric acid got condensed in the spiral tube. F_2 gas was next passed through a tube containing fused sodium fluoride (NaF) which absorbed even the last traces of hydrofluoric acid forming $NaHF_2$. F_2 obtained by this method is pure.

$$2KHF_2 \text{ (In anhydrous } H_2F_2) \longrightarrow 2KF + H_2F_2$$

$$H_2F_2 \rightleftarrows 2H^+ + 2F^-$$

At anode : $F^- - e^- \longrightarrow F;\ F + F \longrightarrow F_2$

At cathode : $H^+ + e^- \longrightarrow H;\ H + H \longrightarrow H_2$

$$2NaF + H_2F_2 \longrightarrow 2NaHF_2$$

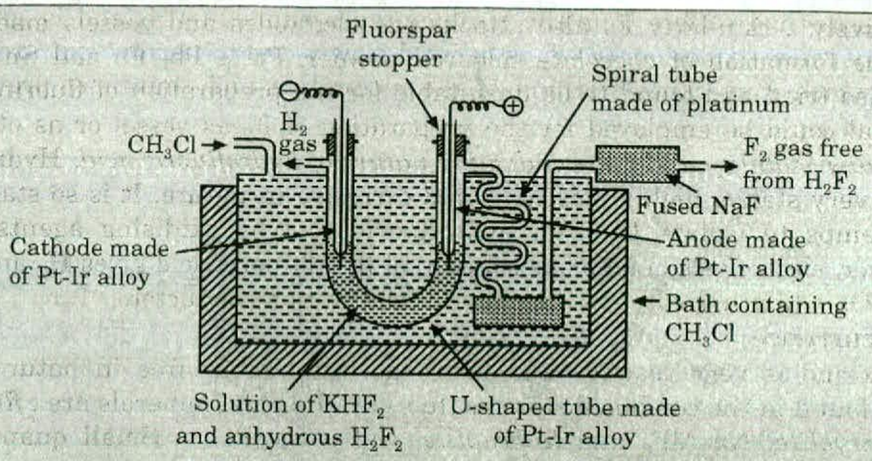


Fig. 38.1. Moissan's method for the isolation of fluorine.

In spite of low temperature *viz.* –23°C employed in this method, there was severe corrosion and wastage of about 5 grams of platinum for the preparation of one gram of F_2. In 1899 he observed that a Cu-tube could be used in place of Pt—Ir tube, since Cu-tube gets coated with a projective layer of CuF_2 which prevents further action of F_2 on Cu, but he continued the use of Pt—Ir electrodes.

2. Deniss Method. This method was devised by *Deniss, Veeder* and *Rockow* in 1931. Essential parts of the electrolytic cell used in this method are : (*a*) *Electrolytic cell.* Electrolytic cell consists of V-shaped tube made of Cu about 2" wide and fitted with copper caps into which graphite electrodes are fixed with bakelite cement The V-shaped copper tube is thickly covered with an insulting layer of asbestos cement. This layer is wound by a resistance wire for heating the V-shaped tube electrically. The whole apparatus is then thickly lagged to prevent the loss of heat. (*b*) *Electrolyte.* Pure and dry KHF_2 (m.pt. = 227°C) is used as an electrolyte. KHF_2 should be perfectly dry, since the presence of traces of moisture results in the formation of O_2 or OF_2. KHF_2 is usually dried in a current of air at 140°–150°C. (*c*) *Electrodes.* Graphite electrodes fixed into the V-shaped copper tube by bakelite cement are used.

Process. When a current of 5 amperes and 12 volts is passed through perfectly dry electrolyte of KHF_2, H_2 is liberated at the cathode and F_2 at the anode and passes out through an exit near the anode (Fig. 38.2). F_2 so produced attacks the copper walls forming the layer of CuF_2 which protects the deeper layers of copper from further attack. The reactions taking place are :

$$2KHF_2 \longrightarrow 2KF + H_2F_2$$

$$H_2F_2 \longrightarrow 2H^+ + 2F^-$$

At cathode : $2H^+ - 2e^- \longrightarrow H_2$

At anode : $2F^- + 2e^- \longrightarrow F_2$

F_2 so obtained is passed through copper tubes containing dry NaF which absorbs HF forming $NaHF_2$

$$2NaF + H_2F_2 \longrightarrow 2NaHF_2$$

This method suffers from the disadvantages namely (*i*) H_2 and F_2 get mixed and may cause explosion. (*ii*) F_2 is evolved slowly due to narrow exit around the anode which may cause frothing of the electrolyte and thus may prevent the escape of F_2.

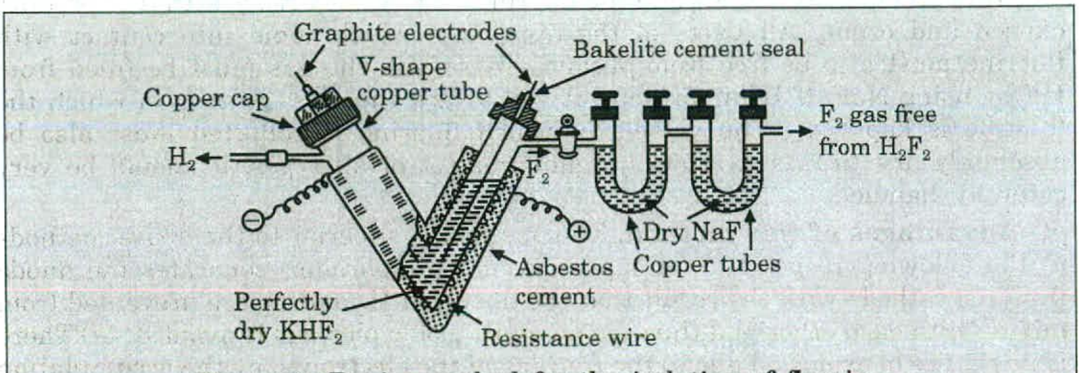


Fig. 38.2. Deniss method for the isolation of fluorine.

3. Whytlaw-Gray's Method. The essential part of the apparatus (Fig. 38.3) used in this method is a copper cell wound with resistance wire for electrical heating. It also acts as the cathode resistance and has an outlet for hydrogen near the top.

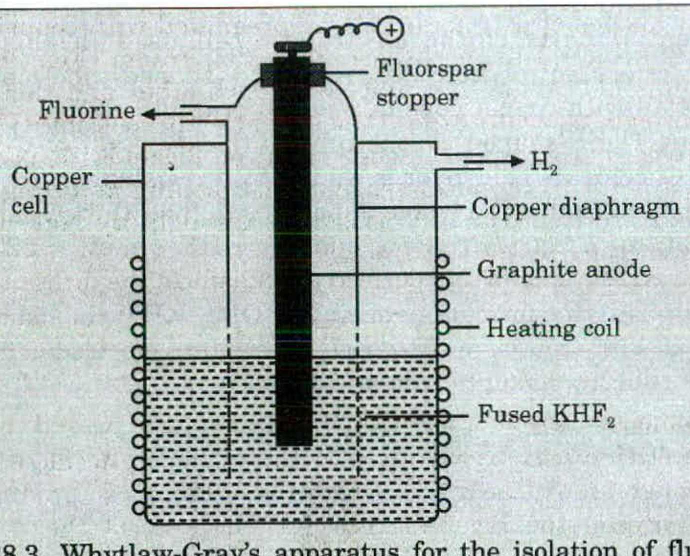


Fig. 38.3. Whytlaw-Gray's apparatus for the isolation of fluorine.

The anode is a rod of graphite enclosed in a copper cylinder. This cylinder has an outlet near the top for the escape of fluorine gas and is perforated near the bottom.

The electrolyte is fused potassium hydrogen fluoride (KHF_2). It undergoes electrolysis to give hydrogen and fluorine.

$$2KHF_2 \longrightarrow 2KF + F_2 + H_2$$

F_2 and H_2 gases escape out of the cell as shown without any possibility of mixing with each other as the anode and the cathode are separated by the cylindrical diaphragm.

Precautions. (*i*) The electrolyte must be absolutely dry, because the presence of moisture hinders electrolysis and the fluorine evolved may react with it to produce oxygen and ozone. All parts of the apparatus which come into contact with fluorine must also be free from oil and grease. (*ii*) The gas must be freed from HF by using NaF. If HF is present, it will attack the glass vessels in which the fluorine is kept. (*iii*) The vessels in which fluorine is collected must also be absolutely dry. (*iv*) As it attacks organic matter of all types, it should be very carefully handled.

Advantages of this method. This method is superior to the above methods in the following respects : (*i*) Copper cylinder (diaphragm) separates the anode from the cathode with the result that the liberated H_2 and F_2 are prevented from mixing with each other and thus the possibility of explosions is avoided. (*ii*) There is no chance of explosion due to the frothing of the electrolyte by the accumulation of gases as the exits for gases are quite wide to allow the gases to escape out quite promptly.

4. Modern Method. The manufacture of F_2 by modern method consists of electrolysing fused KHF_2 mixed with 2 to 3 moles of H_2F_2 at 70-80°C in a rectangle steel vessel using a current of 1000–2000 amperes at 8.5 to 11 volts. The steel vessel acts as a cathode and the anode was earlier made of special graphite form of carbon. Now anodes of petroleum coke impregnated with copper are preferred. A steel cylinder attached to the lid acts as a diaphragm (Fig. 38.4) which does not allow F_2 and H_2 to come in contact with each other and thus the two gases are led out through separate exits. Consequently the possibility of explosion is avoided. The valves used are of monel metal or nickel with packing of teflon, $(C_2F_4)_x$ which is inert to chemical reagents like boiling aqua regia. F_2 obtained at the anode is freed from H_2F_2 by passing it through dry NaF and is stored in steel cylinders in compressed conditions.

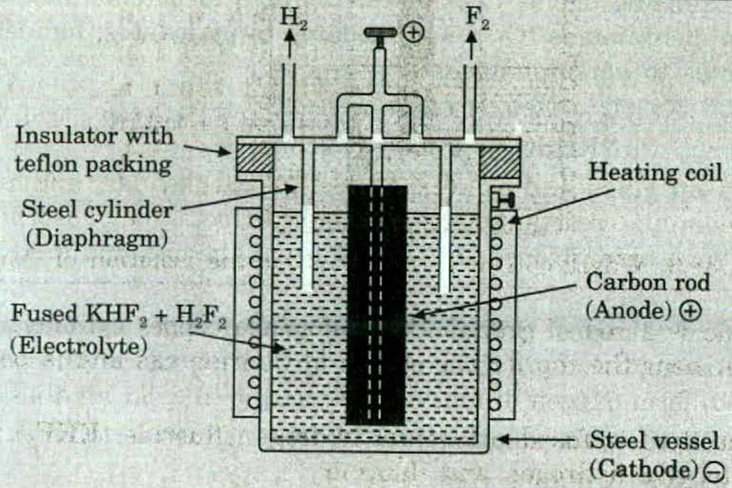


Fig. 38.4. Manufacture of fluorine by modern method.

Physical Properties

Fluorine is a pale yellow gas which condenses to a clear yellow liquid having a density of 1.108 and b.pt. = –187.7°C, and freezes to a pale yellow solid (m.pt. = 223°C). At –252°C the solid becomes colourless. It is a pungent smelling and poisonous gas but less poisonous than HF gas. It attacks organic matter and hence should be handled carefully. Its vapour density is 18.91 which corresponds to the molecular formula F_2.

Chemical Properties

1. Reactivity. Fluorine is the most reactive element as is evident from the fact that it ignites in contact with most of the oxidising substances.

2. Action on halides. When we compare the values of standard reduction potential values (E° values) of halogens corresponding to the reaction :

$$X_2 + 2e^- \longrightarrow 2X^-,$$

we find that E° value for fluorine is the maximum and hence F_2 can displace all the halogens from their halides, *i.e.* F_2 liberates Cl_2 from chlorides, Br_2 from bromides and I_2 from iodides.

3. Combination with elements. Fluorine combines with most metals (*e.g.* Na, Ca, Mg, Al, Ni, Au, Pt etc), non-metals (*e.g.* H, C, 8, P, Cl, Br, I etc.) and metalloids (*e.g.* As, Sb) to form the fluorides.

4. Combination with xenon. Fluorine combines with xenon to form three definite fluorides, XeF_2, XeF_4 and XeF_6. The final product depends on the temperature, pressure and mixing ratio of the constituents.

5. Action of H_2O. F_2 reacts vigorously with H_2O giving O_2 and O_3.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2 \; ; \; 3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

At the same time, some oxygen fluoride (OF_2) is also formed. A jet of steam burns in an atmosphere of F_2 like an illuminating gas.

6. Oxidising action. Since F_2 readily attacks water, giving O_2 and O_3, it acts as a strong oxidising agent. It oxidises chlorates to perchlorates, chromic salts (Cr = + 4) to dichramotes (Cr = + 6), iodates to periodates, halides to halogens and bisulphates to persulphates.

$$KClO_3 + F_2 + H_2O \longrightarrow KClO_4 + H_2F_2$$

$$2KHSO_4 + F_2 \longrightarrow 2HF + K_2S_2O_8$$

7. Action on glass and quartz. F_2 readily attacks glass and quartz forming SiF_4. But when the reactants are thoroughly freed from adsorbed water, the reaction is very slow. Hence dry fluorine can be manipulated in dry glass apparatus.

8. Action of alkalies. Unlike other halogens, F_2 does not form oxy salts with alkalies and no oxy acids of fluorine are known. F_2 reacts with dilute alkalies (2% NaOH) to form oxygen difluoride, OF_2 and with conc. alkalies O_2 is formed.

$$2F_2 + 2NaOH \text{ (2\% solution)} \longrightarrow OF_2 + 2NaF + H_2O$$

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

9. Action of NH_3 and H_2S. F_2 reacts with NH_3 to form N_2 and some NF_3. H_2S burns in an atmosphere of F_2 forming SF_6 and HF.

$$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF$$
$$NH_3 + 3F_2 \longrightarrow NF_3 + 3HF$$
$$H_2S + 4F_2 \longrightarrow SF_6 + 2HF$$

Uses of F_2. (*i*) F_2 is used as an insecticide. (*ii*) It gives a number of compounds which are very useful. Some of the more important compounds and their uses are : (*a*) *Fluorocarbons.* Fluorocarbons like freon-12 and teflon are very useful compounds. For their uses see the properties of fluorine (*Reaction with hydrocarbons and formation of fluoro carbons* as discussed above. (*b*) UF_6 is used in the separation of U^{235} from natural uranium which is used in atom and hydrogen bomb. (*c*) SF_6 has a remarkable property of being a high voltage insulation material and hence is used as an insulating gas in nuclear physics and electrical and X-ray works. (*d*) *Freon,* CCl_2F_2 (*dichlorofluoromethane*) is used in refrigerators and cold storage plants. (*e*) H_2F_2 is used for etching glass, in brewing industry and for removing SiO_2 from iron castings. (*f*) *Cryolite* (Na_3AlF_6) and *fluorspar* (CaF_2) are used in the extraction of Al. (*g*) *Fuorspar* is used in the preparation of H_2F_2. (*h*) *NaF* and Na_3AlF_6 in powdered form are used as insecticides. (*i*) *Presence of small quantities of fluorides*, less than one part per million, in drinking water prevents dental decay. (*j*) *Antimony fluoride* is used in the manufacture of pottery and porcelain and *sodium antimony fluoride* which is a double fluoride of Na and Sb is used as a mordant in the textile industry (*k*) *Sodium fluoro acetate* finds use as rat poison. (*l*) CuF_2 is used in the ceramic industry and as a flux in soldering, welding and blazing. (*m*) MgF_2 is used in optical industry. (*n*) *KF* is widely used in the preparation of fluorocarbons. *Many inorganic fluorine compounds* are used in industry and technology. (*o*) D.D.F.T. which is similar to D.D.T. is an extremely active fungicide and fumigant

Fluorocarbons

F_2 also reacts with hydrocarbons explosively and giver rise to the formation of fluorinated hydrocarbons like CHF_3, CH_2F_2, CHF_3, CF_4, C_2F_8, C_3F_3 etc which are called **fluorocarbons.** The formation of fluorocarbons has been successfully carried out by diluting fluorine with N_2.

Synthesis.

Fluorocarbons can be synthesised :

(*i*) *By the replacement of halogen atom (other than F) in alkyl halides by P-atom in a metal fluoride.* For example :

$$RCl + AgF \longrightarrow AgCl + RF$$

$$C_6H_5PCl_3 + AsF_3 \xrightarrow{25°C} C_6H_5PF_3 + AsCl_3$$

(*ii*) *By the replacement of halogen atom by F-atom in anhydrous HF*

$$CCl_4 \xrightarrow{+HF} \underbrace{CCl_3F + CCl_2F_2 + CClF_3 + CF_4}_{\text{Freons}} + HCl$$

$$CHCl_3 + 2HF \longrightarrow CHCl_2F + 2HCl$$

Chloro-fluorocarbons obtained from CCl_4 are called **freons.** The reactions shown above can be activated by using $SbCl_5$ as catalyst at 50–150°C and pressure of 50–500 lb. inch^{-2}.

(*iii*) *By electrolytic replacement of H_2 by F_2.* In this method organic compounds are subjected to electrolysis in liquid HF at voltage (4–6 volts) below that required for the liberation of F_2. Steel cells are used with Ni anode and steel cathode. Fluorination takes place at anode. This method has been used in laboratory and also as an industrial method.

$$(C_2H_5)_2O \longrightarrow (C_2F_5)_2O$$

$$CH_3COOH \longrightarrow CF_3COOF \xrightarrow{H_2O} CF_3COOH$$

(*iv*) *By the direct replacement of H_2 by F_2.* The reacting compound and F_2 are subjected to electrolytic fluorination in a nitrogen atmosphere. The catalysts used are Cu-gauze, silver-coated copper gauze or caesium fluoride.

$$C_6H_6 + 9F_2 \xrightarrow[265°C]{\text{Cu-gauze}} C_6F_{12} + 6HF$$

Inorganic fluorides such as CoF_3 have also been used for vapour phase fluorination of organic compounds.

$$(CH_3)_3N \xrightarrow{CoF_3} (CH_3)_2FN + (CH_3)F_2N + NF_3$$

Properties and Uses of Fluorocarbons.

(*i*) Chloro-fluorocarbons obtained from CCl_4 are called **freons.** These are used as non-toxic and non-corrosive inert refrigerants, aerosol bomb propellants and heat transfer and fire extinguishing agents. Freons differ from the hydrocarbons in that they are chemically very inert. This property makes them useful solvents, lubricants and insulators.

Difluorodichioromethane, CF_2Cl_2 which is called **freon-12** is used in refrigeration and air conditioning in place of NH_3 and SO_2. It is non-toxic and non-flammable. It is also used as a solvent for D.D.T. and other insecticides.

(*ii*) Just as ethylene (C_2H_4), tetrafluoroethylene (C_2F_4) can also thermally be polymerised to form poly tetrafluoroethylene, $(C_2F_4)_n$. This polymerised compound is called **Teflon.** This is a plastic-like inert material. It is insoluble in any solvent and is not attacked by strong acids, alkalies and oxidizing agents, Due to these properties, this material is used in the construction of chemical plants. It has a very high electrical resistance and is used as an insulating material in cables.

(*iii*) CF_3OF is prepared by the fluorination of CH_3OH or CO by F_2 in presence of AgF_2. It is a stable compound upto 50°C and has been used as a strong oxidising agent.

$$CF_3FO + SO_2 \longrightarrow CF_3OSO_2F$$

$$CF_3FO + SO_3 \longrightarrow CF_3OOSO_2F$$

$$CF_3OF + SF_4 \longrightarrow CF_3OSF_5.$$

Conceptual Questions with Answers

Q.1 Explain why it is not possible to obtain F_2 by the electrolysis of aqueous NaF

or Explain why the electrolysis of KBr(aq) gives Br_2 at anode but the electrolysis of KF(aq) does not give F_2.

Ans : On electrolysis, the aqueous solution of NaF gives Na metal on cathode and F_2 on anode.

$$NaF \rightleftharpoons Na^+ + F^-$$

$$F^- \longrightarrow F + e^-,\ F + F \longrightarrow F_2 \ (\textit{At anode})$$

$$Na^+ + e^- \longrightarrow Na \ (\textit{At cathode})$$

Now, since F_2 is a strong O.A., F_2 obtained at anode is consumed in oxidising H_2O (to O_2) present in the aqueous solution of NaF.

$$\begin{array}{ccccccc} 2F_2 & + & 2H_2O & \longrightarrow & O_2 & + & 4HF \\ (F = 0) & & (O = -2) & & (O = 0) & & (F = -1) \\ (OA) & & & & & & \end{array}$$

F_2 also produces O_3 with H_2O.

$$3F_2 + 3H_2O \longrightarrow O_3 + 6HF$$

Thus at anode, we get ozonised O_2 instead of F_2.

Q.2 Write the balanced chemical equation for the reaction between Cl_2 and hot and conc. NaOH. Justify that this reaction is a disproportionation reaction.

Ans : $$\begin{array}{ccccccc} 3Cl_2 + 6NaOH\ (\textit{conc}) & \xrightarrow{\text{Hot}} & 5NaCl & + & NaClO_3 & + & 3H_2O \\ (Cl = 0) & & (Cl = -1) & & (Cl = +5) & & \end{array}$$

It is obvious from the reaction that the O.S. of Cl decreases from zero to –1 in NaCl and increases from zero to +5 in $NaClO_3$. Hence this reaction is a disproportionation reaction.

Q.3 Addition of Cl_2 to KI solution gives a brown colour but excess of Cl_2 turns it colourless. Explain with reasons.

Ans : Since Cl_2 is stronger O.A. than I_2, it oxidises I^- ion to I_2 when Cl_2 is a added to KI solution.

$$\begin{array}{ccccccc} Cl_2 & + & KI\ (aq) & \longrightarrow & 2KCl\ (aq) & + & I_2 \ (\textit{Brown colour}) \\ (Cl = 0) & & (I = -1) & & (Cl = -1) & & (I = 0) \end{array}$$

If Cl_2 gas is passed in excess, then Cl_2 oxidises I_2 evolved in the above reaction to iodic acid (HIO_3) which is colourless.

$$\begin{array}{ccccccccc} 5Cl_2 & + & I_2 & + & 6H_2O & \longrightarrow & 10HCl & + & 2HIO_3 \ (\textit{Colourless}) \\ (Cl = 0) & & (I = 0) & & & & (Cl = -1) & & (I = +5) \end{array}$$

or $$5Cl_2 + I_2 + 6H_2O \longrightarrow 10Cl^- + 2IO_3^- + 12H^+$$

Q.4 How can you prepare Cl_2 from HCl and HCl from Cl_2. Write reactions only.

Ans : HCl can be oxidised to Cl_2 by a number of oxidising agents such as MnO_2, $KMnO_4$, $K_2Cr_2O_7$, etc.

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

Cl_2 can be reduced to HCl by reaction of H_2 in presence of diffused sunlight.

$$H_2 + Cl_2 \xrightarrow{\text{Diffused sunlight}} 2HCl$$

Q.5 Sea is the greatest source of halogens. Comment.

Ans : Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but mainly sodium chloride (2.5% by mass). Dried up sea beds contain sodium chloride and carnallite, $KCl.MgCl_2.6H_2O$. Certain seaweeds contain upto 0.5% of iodine as sodium iodide and chile saltpetre ($NaNO_3$) contains upto 0.2% of sodium iodate. Thus, sea is the greatest source of halogens.

Q.6 Write the reactions of F_2 and Cl_2 with water.

Ans : F_2 being a strong oxidising agent oxidises H_2O to O_2 or O_3.

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

$$3F_2(g) + 3H_2O(l) \longrightarrow 6H^+\,(aq) + 6F^-\,(aq) + O_3(g)$$

Cl_2 on the other band, reacts with H_2O to form hydrochloric acid and hypochorous acid

$$Cl_2(g) + H_2O(l) \longrightarrow \underset{\text{Hydrochloric acid}}{HCl\,(aq)} + \underset{\text{Hpochlorous acid}}{HOCl\,(aq)}$$

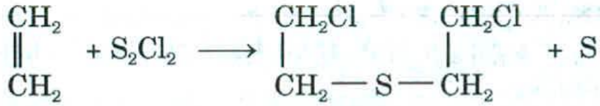
Q.7 Name two poisonous gases which can be prepared from chlorine gas.

Ans : Two poisonous gases which can be prepared from Cl_2 are : (*i*) phosgene (*ii*) mustard gas. These are prepared as follows :

(*i*) $CO + Cl_2 \xrightarrow{h\nu,\ \text{charcoal}} \underset{\text{Phosgene}}{COCl_2}$

(*ii*) Cl_2 is passed through boiling S, when S_2Cl_2 is formed. This when reacted with ethene gives mustard gas.

$$\underset{\text{(Boiling)}}{S_8} + 4Cl_2 \longrightarrow \underset{\text{Sulphur monochloride}}{4S_2Cl_2}$$



$$\underset{\text{Ethene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} + S_2Cl_2 \longrightarrow \underset{\text{Mustard gas}}{\begin{matrix}CH_2Cl & & CH_2Cl\\ | & & |\\ CH_2 & -S- & CH_2\end{matrix}} + S$$

Ethene Mustard gas

Q.8 Give a chemical method for the preparation of F_2.

Ans : F_2 can be obtained by the reaction between pot.

hexafluoromagnate (IV), K_2MnF_6 and SbF_5

$$2K_2MnF_6 + 4SbF_5 \longrightarrow 2K^+[SbF_6]^- + MnF_3 + F_2$$

Above reaction takes place through the following steps :

$$2KMnF_6 \longrightarrow 2K^+ + 2F^- + MnF_4\ ] \times 2$$

$$SbF_5 + F^- \longrightarrow SbF_6^-\ ] \times 4$$

$$2MnF_4 \longrightarrow 2MnF_3 + F_2$$

$$2K_2MnF_6 + 4SbF_5 \longrightarrow 4K^+ + 4SbF_6^- + 2MnF_3 + F_2$$

or $2K_2MnF_6 + 4SbF_5 \longrightarrow 4K^+[SbF_6]^- + 2MnF_3 + F_2$

Q.9 Chlorine water has both oxidising as well as bleaching properties. Explain.

Ans : In presence of moisture or water, Cl_2 gives nascent oxygen which is responsible for its oxidising and bleaching properties as shown below :

$$Cl_2 + H_2O \longrightarrow [HCl + HClO] \longrightarrow 2HCl + \underset{\text{Nascent oxygen}}{[O]}$$

(*i*) It oxidises acidified ferrous sulphate to ferric sulphate

$$\begin{array}{rcl} Cl_2 + H_2O & \longrightarrow & 2HCl + O \\ 2FeSO_4 + H_2SO_4 + O & \longrightarrow & Fe_2(SO_4)_3 + H_2O \\ \hline 2FeSO_4 + H_2SO_4 + Cl_2 & \longrightarrow & Fe_2(SO_4)_3 + 2HCl \\ \textit{(Green)} & & \textit{(Brown)} \end{array}$$

(*ii*) It bleaches vegetable and organic colouring matter to colourless substances by oxidation.

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

Vegetable colouring matter + O ⟶ Oxidised colourless substances.

Q.10 (*a*) Why does chlorine water lose its yellow colour on standing?

(*b*) What happens when Cl_2 reacts with cold dilute solution of sodium hydroxide? Write equations only.

Ans : (*a*) Chlorine water is yellow due to the presence of hypochlorous acid (HClO) in it. On standing, HClO, being unstable, decomposes to form HCl. As a result, yellow colour disappears.

$$Cl_2 + H_2O \longrightarrow HCl + \underset{\textit{(Yellow)}}{HClO} \longrightarrow \underset{\textit{(Colourless)}}{2HCl} + [O]$$

(*b*) With cold dilute NaOH solution, Cl_2 gives a mixture of sodium chloride (NaCl) and sodium hypochlorite (NaClO)

$$2NaOH\ (\mathit{dil.}) + Cl_2 \xrightarrow{\text{Cold}} NaCl + NaClO + H_2O$$

Q.11 What is superhalogen ? What happens when this halogen reacts with a cold solution of NaOH ?

Ans : F_2 is called superhalogen. It is so called because it differs from other halogens in many properties. For example it has highest electronegativity, smallest size, highest E° value, no vacant *d*-orbitals in its valence shell etc.

When F_2 reacts with NaOH, OF_2 is obtained.

$$2F_2 + 2NaOH \longrightarrow OF_2 + 2NaF + H_2O$$

Q.12 How will you prepare : (*a*) Cl_2 gas in the laboratory (*b*) Br_2 from sea water.

Ans : (*a*) Chlorine gas is prepared in the laboratory by heating a mixture of manganese dioxide (MnO_2) and conc. HCl.

$$MnO_2\ (s) + 4HCl\ (aq) \xrightarrow{\Delta} MnCl_2\ (aq) + Cl_2\ (g) + H_2O(l)$$

(*b*) Br_2 is manufactured from sea water by passing Cl_2 through it.

$$2Br^-\ (aq) + Cl_2\ (g) \longrightarrow Br_2\ (l) + 2Cl^-\ (aq)$$

University Questions

1. What were the difficulties encountered in the isolation of fluorine? How were these overcome? *(Agra 89)*
2. Write the names of chief ores of fluorine. Describe the modern methods for the isolation of this element. *(Meerut 85, 86; Sambalpur 8; Utkal 85; Jiwaji 84; Agra 89)*
3. Write a note on "Fluorocarbons". *(Meerut 85)*
4. Describe how Cl_2 is prepared on a large scale. Mention its important uses. *(Delhi Hons. 78 S)*
5. What are the important sources of Br_2? How is it obtained on a large scale? *(Punjab 86)*
6. How is iodine manufactured?*(Punjab 86; Kurukshetra 85; Hyderabad 86)*
7. Write a short note on "Basic iodine". *(Raj. 84, 86, 87; Madras 85, 86)*
8. Explain the following :
    (*i*) F is a non-metal while I shows metallic character.
    (*ii*) A we go down the column of halogens, there is an increase in the metallic character of the halogens.
9. Describe the action of heat on HBr and conc. H_2SO_4. *(Delhi 99)*
10. What is main source of fluorine ? Give modern method for the isolation of fluorine. *(Gorakhpur 99, Allahabad 99)*
11. Write a note on "Anomalous behaviour of fluorine". *(Lucknow 2000)*
12. Discuss the difficulties met in the isolation of fluorine. Describe the modern method for its isolation. *(Avadh 2000)*

CHAPTER

39

Halogen Acids : Hydracids or Hydrogen Halides

All the halogens combine with hydrogen and form the volatile covalent hydrides of HX type (X = F, Cl, Br and I) in which the halogen (X) shows an oxidation state of –1. These hydrides are called by various names like **hydrogen acids, hydracids, hydrohalic acids and hydrogen halides.** The salts of these acids are called **halides.** General methods of the preparation and properties of these acids have already been discussed in chapter 43. The four halogen acids given by halogens are *hydrofluoric acid*, H_2F_2; *hydrochloric acid*, HCl; *hydrobromic acid*, HBr and *hydroiodic acid*, HI. Now these acids are discussed separately as below.

Hydrofluoric Acid, H_2F_2

This acid is an associated molecule and hence is represented as H_2F_2.

Preparation

Pure anhydrous acid is prepared by distilling dry KHF_2 in a platinum, copper or steel vessel cooled in freezing mixture (laboratory preparation) or by passing dry H_2 over dry AgF.

$$2KHF_2 \longrightarrow H_2F_2 + 2KF; \; 2AgF + H_2 \longrightarrow H_2F_2 + 2Ag$$

An aqueous solution of hydrofluoric acid is mannfatured by heating calcium fluoride, CaF_2 (*fluorspar*) with 90% H_2SO_4

$$CaF_2 + H_2SO_4 \longrightarrow H_2F_2 + CaSO_4$$

The vapours of hydrofluoric acid are often dissolved in water contained in a lead receiver and coated on the inside by wax to get an aqueous solution of hydrofluoric acid.

Storage of the Acid

The anhydrous acid is stored in well-cooled platinum, gold or silver vessels or steel cylinders. The commercial aqueous acid is kept in gutta-percha bottles when dilute and in ceresin wax bottles when concentrated.

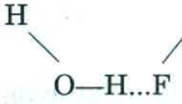
Physical Properties

Anhydrous acid is a colourless, strongly fuming liquid which boils at 194°C and freezes at –83°C. It is extremely poisonous and dangerous to handle, as in contact with skin it forms ulcerated sores. It is highly soluble in water and forms a constant boiling mixture containing 36% of the acid which boils at 120°C. The anhydrous acid is a bad conductor of electricity. The liquid acid and its vapour at low temperatures consist of polymeric form, $(HF)_x$ whereas at 90°C the vapour density has the normal value.

Chemical Properties

***(i)* Combustibility.** H_2F_2 is neither combustible nor supporter of combustion.

***(ii)* Acidic nature.** It is a weak dibasic acid (even weaker than H_3PO_4 but stronger than HNO_2) and hence forms two types of salts namely *normal salts* (*e.g.* NaF) and *acid salts* (*e.g.* $NaHF_2$) The formation of acid salts is due to the fact that aqueous solution of the acid contains hydrogen-bonded species like



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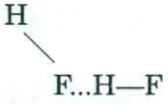


Note that acid salts are not given by other halogen acids.

***(iii)* Action on metals.** Anhydrous acid does not attack any metal under ordinary conditions except potassium while aqueous concentrated solution of the acid attacks most of metals (*e.g.* Na, Ag, Al, Ca, Sc, Zn, Mg) forming their fluorides with the liberation of H_2 gas.

***(iv)* Action on oxides, hydroxides, carbonates etc.** Concentrated aqueous solution of the acid reacts with these species to form the fluorides. For example :

$$B_2O_3 + 3H_2F_2 \longrightarrow 2BF_3 + 3H_2O$$

$$2NaOH + H_2F_2 \longrightarrow 2NaF + H_2O$$

$$CaCO_3 + H_2F_2 \longrightarrow CaF_2 + H_2O + CO_2$$

Reaction of the concentrated aqueous solution of the acid with silica (SiO_2) is of importance. In this reaction H_2SiF_6 is formed.

$$SiO_2 + 3H_2F_2 \longrightarrow H_2SiF_6 + 2H_2O$$

Since glass contains SiO_2, H_2F_2 cannot be kept in glass containers.

***(v)* Action on glass.** Pure anhydrous acid does not attack glass but a concentrated aqueous solution of the acid attacks glass. In this reaction H_2F_2 reacts with silica (SiO_2), sodium silicate (Na_2SiO_3) and calcium silicate ($CaSiO_3$) which are the constituents of glass, forming SiF_4 and H_2SiF_6 and its salts.

(*a*) *With* SiO_2 : $SiO_2 + 3H_2F_2 \longrightarrow H_2SiF_6 + 3H_2O$

(*b*) *With* Na_2SiO_3 : $Na_2SiO_3 + 3H_2F_2 \longrightarrow Na_2SiF_6 + 3H_2O$

(*c*) *With* $CaSiO_3$: $CaSiO_3 + 3H_2F_2 \longrightarrow CaSiF_6 + 3H_2O$

The etching of glass is based on the above reactions. For this purpose commercial H_2F_2(40–60%) is used.

***(vi)* Action of $AgNO_3$ and $BaCl_2$ solutions.** With $AgNO_3$ solution, it gives no precipitate since AgF formed is soluble in water (*cf.* other halogen acids). With $BaCl_2$ solution, it forms a white precipitate of BaF_2 which is insoluble in dil. HNO_3 but soluble in conc. HCl (difference from other halogen acids)

$$H_2F_2 + 2AgNO_3 \longrightarrow \underset{\text{(Soluble in water)}}{2AgF} + 2HNO_3$$

$$H_2F_2 + BaCl_2 \longrightarrow \underset{\text{ppt.}}{BaF_2} + 2HCl$$

***(vii)Stability*.** H_2F_2 is extremely stable and is not oxidised by strongly oxidising agents or decomposed by heat. Thermal stability is due to the strength of H—F bond in H_2F_2 molecule.

Etching of Glass by H_2F_2

In etching, glass surface is covered with a thin film of paraffin wax and the design to be produced is scratched through the film with a sharp needle. The surface is then exposed to the action of the gas or of an aqueous solution (40–60%) of the acid. The paraffin coating protects the unexposed glass. Burettes, thermometers and other glass wares are engraved in this manner. Etching with solution is clear but it is opaque with the gas.

Uses

H_2F_2 is used : (*i*) In the etching of glass and making scales on the glass instruments. (*ii*) As an antiseptic in dyeing and brewing industries, since its effect on yeast is very little as compared with its action on other organisms. (*iii*) In the manufacture of fluorine. (*iv*) In the manufacture of a class of fluorine-containing dyes that have proved very fast and remarkably resistant to light. (*v*) In the pickling of alloy steels. (*vi*) In the manufacture of fluorine-containing plastics like Teflon etc. which are characterised by extreme chemical inertness, high thermal stability and very good dielectric properties. (*vii*) Because of its action on silica H_2F_2 is extensively used for removing silica from artificial graphite and Swedish filter paper. (*viii*) By the action of H_2F_2 on sodium aluminate, *synthetic* (*artificial*) *cryolite* is prepared. H_2F_2 is also used for the preparation of AlF_3. Both these substances are used in the metallurgy of aluminium. (*ix*) H_2F_2 is also used in the production of uranium hexafluoride (UF_6) which, because of its thermal stability and sufficiently high vapour pressure at the room temperature, is employed for the separation of uranium isotopes by the gaseous diffusion process. UF_6 is prepared by the action of H_2F_2 on U_2O_3 to get UF_3 which is then treated with F_2 to get UF_6 (*x*) Fluorides of alkali metals and antimony are used as mordant in dyeing industry. (*xi*) H_2F_2 is also used as a refrigerant in many of the cooling processes.

Structure

The vapour density of hydrofluoric acid measured near about its boiling point *viz.* 30°C indicates the formula H_2F_2. Measurement of the lowering of freezing point of water by hydrogen fluoride compounds gives a molecular formula H_2F_2 in aqueous solutions. The formula of the salts like KHF_2 also confirms this view. It may, therefore, be concluded that the hydrofluoric acid vapour just above the boiling point may be a mixture of H_2F_3, H_2F_2 and HF molecules but as the temperature rises, more and more dissociation takes place but at 100°C it is only monomeric. In concentrated aqueous solutions the molecule is represented as H_2F_2. Dilute solutions and the vapour above 88°C are mostly composed of HF molecules.

Comparison of H_2F_2 with Other Halogen Acids

(1) Acid strength. All the halogen acids ionise in aqueous solution and hence behave as acids. H_2F_2 ionises only slightly while other acids ionise completely. Hence H_2F_2 is the weakest acid of all the acids.

(2) Ionic character of H—X bond. H—F bond in H_2F_2 acid has the highest degree of polarity, since F atom has the highest value of electronegativity of all the halogen atoms.

(3) Physical state. H_2F_2 is a liquid at ordinary temperature while other halogen acids are colourless gases.

(4). Reducing property. H_2F_2 has no reducing property while other acids are good reducing agents.

(5) Hydrogen bonding and formation of acid salts. Aqueous solution of HF contains hydrogen bonded species. On account of the presence of H-bonding in HF molecule, this molecule forms acid salts of KHF_2 type which contains the anion $[F—H...F]^-$. No such acid salts are given by other HX acids, since other acids have no hydrogen bonding. The occurrence of H-bonding between HF molecules is due to the high electronegativity and small size of F-atom. No hydrogen bonds are formed between HCl, HBr and HI molecules, since Cl, Br and I atoms in these molecules are much less electronegative and larger in size than F-atom.

(6) Action on silica or glass. Strong solution of H_2F_2 attacks silica or glass readily forming SiF_4 which gives complex fluosilicic acid, H_2SiF_6 with excess of H_2F_2. Other halogen acids do not act upon silica or glass.

$$SiO_2 + 2H_2F_2 \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + H_2F_2 \longrightarrow H_2SiF_6.$$

(7) Action on metals. All the halogen acids react with metals like Zn and Mg to form H_2. The action of H_2F_2 on metals is, however, less violent than with other halogen acids.

(8) Action of mixture of MnO_2 and H_2SO_4. When H_2F_2 is heated with a mixture of MnO_2 and H_2SO_4, no gas is evolved. On the other hand, in case of HCl, HBr and HI acids, Cl_2 (greenish-yellow), Br_2 (reddish brown vapour) and I_2 (violet vapour) gases are evolved.

(9) Action of $AgNO_3$ solution. With $AgNO_3$ solution, H_2F_2 gives no precipitate, since AgF formed is soluble in water. On the other hand, HCl, HBr and HI give the precipitates of AgCl (white), AgBr (pale yellow) and AgI (yellow).

$$H_2F_2 + 2AgNO_3 \longrightarrow 2AgF \text{ (soluble)} + 2HNO_3$$

$$HX(X = Cl, Br, I) + AgNO_3 \longrightarrow AgX \text{ (coloured ppt.)} + HNO_3$$

(10) Action of $BaCl_2$ solution. With $BaCl_2$ solution, H_2F_2 gives a white precipitate of BaF_2 while other halogen acids do not give any precipitate, since BaX_2(X = Br and I) formed are soluble.

$$H_2F_2 + BaCl_2 \longrightarrow BaF_2 \text{ (white ppt)} + 2HCl$$

$$2HX(X = Br, I) + BaCl_2 \longrightarrow BaX_2 \text{ (soluble)} + 2HCl$$

(11) Action of $Pb(CH_3COO)_2$ solution. H_2F_2 gives no precipitate with $Pb(CH_3COO)_2$ solution while other halogen acids give the precipitates of $PbCl_2$ (white), $PbBr_2$ (white) and PbI_2 (yellow) respectively.

(12) Dissocation. H_2F_2 does not dissociate on heating while other halogen acids dissociate at definite temperatures.

Similarities between HF and H_2O

(*i*) Both the compounds resemble each other in solubility, fusibility etc.

(*ii*) Both form associated molecules, $(HF)_x$ and $(H_2O)_x$. The formation of such molecules is due to hydrogen bonding in HF and H_2O molecules.

(*iii*) The boiling point of HF is exceptionally high in comparison to those of other hydrogen halides. (H_2F_2 = 19.4°C, HCl = –85°C, HBr = –67°C, HI = –36°C). Similarly the boiling point of H_2O is also exceptionally high in comparison to those of H_2S and H_2Se (H_2O = 100°C, H_2S = –61.8°C, H_2Se = –42°C). Just as the exceptionally high boiling point of HF is ascribed due to strong H-bonds between HF molecules, the high boiling point of H_2O is also attributed to the H-bonds between H_2O molecules.

(*iv*) Like H_2O, H_2F_2 is a weak acid and both are ionising solvents.

(*v*) Heats of formation of H_2F_2 and H_2O are close to each other.

Hydrochloric Acid, HCl

Manufacture

Large quantities of commercial HCl today are being obtained by the synthesis method which is based on the direct combination of hydrogen with chlorine in accordance with the equation :

$$H_2 + Cl_2 \rightleftharpoons 2HCl + 44{,}000 \text{ K.cals.}$$

This reaction is very slow under ordinary conditions but proceeds very smooth in the presence of high temperatures and sunlight. Both the gases, *viz.*, H_2 and Cl_2 are obtained as by-products during the manufacture of NaOH by the electrolysis of a solution of NaCl. Hence the process is quite economical. In this process pure electrolytic chlorine is burnt in an atmosphere of electrolytic hydrogen in large vertical silica tubes. The acid obtained by this process is quite pure.

Physical Properties

It is a colourless gas, heavier than air with pungent smell and acidic taste. It is extremely soluble in water and fumes strongly in moist air. 450 volumes of the gas dissolve in one volume of water. The gas can be easily liquefied and the liquid so produced boils at –83°C and freezes to a white crystalline solid at –11.3°C. It forms a constant boiling mixture with water when it contains 22.2 per cent of the acid. The mixture boils at 110°C. Dilute solution of the acid cannot, therefore, be concentrated by boiling beyond 22.2 per cent.

Chemical Properties

(*i*) Dissociation. HCl is quite stable but dissociates to give H_2 and Cl_2 at about 1500°C.

$$2HCl \longrightarrow H_2 + Cl_2$$

(*ii*) Action on litmus paper. Hydrogen chloride does not affect litmus in the absence of moisture but in the moist state or in solution it turns blue litmus red. This is due to the fact that it dissolves in water to give hydrochloric acid.

(*iii*) Combustibility. It is neither combustible nor a supporter of combustion.

(*iv*) Action on NH_3. It forms dense white fumes of ammonium chloride with ammonia.

$$HCl + NH_3 \longrightarrow NH_4Cl$$

(*v*) Acidic nature. The solution of the gas is highly acidic and one of the strongest acid. It reacts with metals like iron, zinc, with sodium, potassium and calcium, forming the corresponding *chlorides* with the evolution of hydrogen. HCl gas also reacts with metals like zinc, aluminium, tin etc., when heated, forming *anhydrous chlorides.*

(*vi*) Action on oxides, hydroxides, carbonates and bicarbonates. HCl neutralises oxides and hydroxides while carbonates and bicarbonates get decomposed with the evolution of CO_2. For example :

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O;\ NaOH + HCl \longrightarrow NaCl + H_2O$$

$$2HCl + No_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2;\ HCl + NaHCO_3 \longrightarrow NaCl + H_2O + CO_2$$

(*vii*) Action of oxidising agents. HCl gets oxidised to Cl_2 by oxidising agents like MnO_2, $KMnO_4$, $K_2Cr_2O_7$ and PbO_2.

(*viii*) Precipitation reactions. When HCl is added to the solution of a soluble salt of Ag (I), Pb (II) and Hg (I), AgCl, $PbCl_2$ and Hg_2Cl_2 are precipitated.

(*ix*) Formation of aqua regia. HCl forms aqua regia with HNO_3 when mixed in the ratio of 3 : 1.

$$3HCl + HNO_3 \longrightarrow NOCl + 2Cl + 2H_2O$$

Uses

(*i*) Hydrochloric acid is used in the manufacture of chlorides and chlorine. (*ii*) It is used in the textile and dyeing industries, as also in tanning. (*iii*) In the form of *aqua regia* it is used for dissolving metals like gold and platinum. (*iv*) It is used as an important reagent in the laboratory. (*v*) It is also used in medicine. (*vi*) It is also used for cleaning iron sheets during tin plating, galvanisation etc. (*vii*) It is also used for the extraction of glue from animal tissues and bones.

Hydrobromic Acid, HBr

Preparation

HBr can be prepared by passing a mixture of H_2 and Br_2 over a platinum spiral heated to redness by an electric current or its aqueous solution can be obtained by passing SO_2 or H_2O through Br_2 water.

$$H_2 + Br_2 \longrightarrow 2HBr;\ Br_2 + H_2S \longrightarrow 2HBr + S$$

$$Br_2 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2HBr$$

Physical Properties

Hydrogen bromide is a colourless pungent smelling gas heavier than air. It is very soluble in water and fumes strongly in moist air. At low temperature and high pressure it is changed to a liquid which boils at – 67°C and solidifies at –87°C. It forms a constant boiling mixture at 126°C when it contains 48% of the gas in solution.

Chemical Properties

***(i)* Action on litmus.** Dry HBr has no action on litmus but moist gas turns it red.

***(ii)* Combustibility.** It is neither combustible nor a supporter of combustion.

***(iii)* Acidic nature.** It reacts with metals like zinc, iron and tin to give hydrogen gas. It is a monobasic acid and reacts with alkalies, carbonates and oxides to give *bromides.*

$$Zn + 2HBr \longrightarrow ZnBr_2 + H_2$$
$$Na_2CO_3 + 2HBr \longrightarrow 2NaBr + H_2O + CO_2$$
$$NaOH + HBr \longrightarrow NaBr + H_2O$$

***(iv)* Action with ammonia.** With concentrated ammonia solution, white fumes of ammonium bromide are produced.

$$NH_3 + HBr \longrightarrow NH_4Br$$

***(v)* Reducing action.** It is more easily decomposed than hydrochloric acid and as such acts as a *reducing agent.* Sulphuric acid, hydrogen peroxide and air oxidise it to bromine.

$$H_2SO_4 + 2HBr \longrightarrow Br_2 + SO_2 + 2H_2O$$
$$2HBr + H_2O_2 \longrightarrow Br_2 + 2H_2O$$
$$4HBr + O_2 \text{ (From air)} \longrightarrow 2Br_2 + 3H_2O.$$

***(vi)* Action with $AgNO_3$ and $Pb(CH_3COO)_2$.** With silver nitrate it gives a pale yellow precipitate insoluble in nitric acid and sparingly soluble in ammonium hydroxide. With lead acetate it gives a white precipitate soluble in hot water.

$$HBr + AgNO_3 \longrightarrow \underset{\text{Pale yellow ppt.}}{AgBr} + HNO_3$$
$$2HBr + (CH_3COO)_2Pb \longrightarrow \underset{\text{White ppt.}}{PbBr_2} + 2CH_3COOH$$

***(vii)* Action of halogens.** Bromine is liberated from hydrobromic acid by fluorine and chlorine but iodine has no action.

$$2HBr + X_2(X = F, Cl) \longrightarrow 2HX + Br_2$$

Uses

HBr is an important laboratory regent and is used in preparing bromo derivatives of unsaturated organic compounds and some inorganic bromides. AgBr and KBr are used in photography and in medicine.

Hydroiodic Acid, HI

Preparation

HI can be prepared by the reactions shown below :

$$H_2 + I_2 \rightleftharpoons 2HI$$
$$2P + 3I_2 + 3H_2O \longrightarrow H_3PO_3 + HI \text{ (\textit{Laboratory preparation})}$$
$$H_2S + I_2 \longrightarrow 2HI + S$$
$$SO_2 + I_2 + 2H_2O \longrightarrow 2HI + H_2SO_4$$

Physical Properties

Hydrogen iodide is a colourless, pungent smelling gas, heavier than air and highly soluble in water. Like other halogen hydracids, it fumes in moist air and can be liquefied (b. pt. –35.5°C) and solidified (m. pt. –50.8°C). It forms a constant boiling mixture at 127°C when the solution contains 57% of hydrogen iodide.

Chemical Properties

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

***(ii)* Solubility.** HI gas is highly soluble in water like HCl or HBr. The solution saturated at 10°C contains 70% of HI by weight. The solution fumes strongly in air and is acidic in nature. Thus the solution reacts with alkalies and bicarbonates to form salts called *iodides.*

$$NaOH + HI \longrightarrow NaI + H_2O$$

$$NaHCO_3 + HI \longrightarrow NaI + H_2O + CO_2$$

The solution is colourless when prepared but turns brown on keeping owing to the formation of free I_2 by the oxidation of HI.

$$4HI + O_2 \longrightarrow 2H_2O + 2I_2$$

***(iii)* Action on NH_3.** White fumes of NH_4I are obtained.

$$NH_3 + HI \longrightarrow NH_4I$$

***(iv)* Action on halogens.** F_2, Cl_2 or Br_2 liberate I_2 when passed through an aqueous solution of HI.

$$2HI + X_2(X_2 = F_2, Cl_2 \text{ or } Br_2) \longrightarrow 2HX + I_2$$

***(v)* Stability.** HI is the least stable of all the halogen acids and decomposes into H_2 and I_2 in sunlight or on heating.

$$2HI \rightleftharpoons H_2 + I_2$$

***(vi)* Reducing properties.** HI is the most powerful reducing agent among all the halogen acids. During this reaction HI is itself oxidised to free I_2. Thus HI reduces O_2 to H_2O, H_2O_2 to H_2O, Fe(III) salts to Fe(II) salts, HNO_2 to NO, $SnCl_4$ to $SnCl_2$, H_2SO_4 to SO_2,S or H_2S, HNO_3 to NO_2, HIO_3 to I_2, acidified $KMnO_4$ solution to $MnSO_4$, acidified $K_2Cr_2O_7$ to $Cr_2(SO_4)_3$ and Cl_2 to HCl.

***(vii)* Reaction with salts.** HI gives a yellow precipitate of AgI with $AgNO_3$ solution. With the solutions of $Pb(CH_3COO)_2$, $CuSO_4$ and $HgCl_2$, HI gives the pricipitates of PbI_2 (yellow), CuI and HgI_2 (scarlet) respectively. Here it may be noted that HF, HCl and HBr do not react with $CuSO_4$ and $HgCl_2$ solutions.

Conceptual Questions with Answers

Q.1 How will you prepare : *(a)* HF from CaF_2 *(b)* HBr from NaBr.

Ans : (*a*) HF is prepared by heating a mixture of calcium fluoride and conc. H_2SO_4.

$$CaF_2\ (s) + H_2SO_4\ (l) \xrightarrow{\Delta} CaSO_4\ (s) + 2HF\ (g)$$

(*b*) NaBr on heating with a non-oxidising acid such as H_3PO_4 gives HBr.

$$3NaBr\ (s) + H_3PO_4\ (l) \xrightarrow{\Delta} 3HBr\ (g) + Na_3PO_4\ (s)$$

Q.2 Name the products formed by the action of conc. H_2SO_4 on (*i*) CaF_2 (*ii*) NaCl (*iii*) NaBr and (*iv*) NaI.

Ans : (*i*) $CaF_2 + H_2SO_4 \xrightarrow{\Delta} CaSO_4 + \boxed{2HF}$

(*ii*) $2NaCl + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + \boxed{2HCl}$

(*iii*)
$$\begin{array}{l} 2NaBr + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2HBr \\ 2HBr + H_2SO_4 \longrightarrow SO_2 + 2H_2O + Br_2 \\ \hline 2NaBr + 2H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + 2H_2O + \boxed{Br_2} \end{array}$$

(*iv*)
$$\begin{array}{l} 2NaI + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2HI \\ 2HI + H_2SO_4 \longrightarrow SO_2 + 2H_2O + I_2 \\ \hline 2NaI + 2H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + 2H_2O + \boxed{I_2} \end{array}$$

University Questions

1. How is hydrofluoric acid prepared? (*Raj. 87; Meerut 88; Utkal 86*)
2. Discuss the properties of HF. (*Raj. 87; Meerut 88*)
3. Discuss the uses and structure of HF. (*Meerut 88*)
4. Give reasons for the following :
   (*i*) HF cannot be stored in glass bottles. (*Burdwan 86; Poona 85; Meerut 84*)
   (*ii*) Aqueous solution of HF_2 on electrolysis, does not give fluorine at anode. (*Delhi 87*)
   (*iii*) The solutions of organic compounds in HF become conductive. (*Raj. 86 S*)
5. Describe with the help of a neat diagram the manufacture of HCl. How is it purified? (*Punjab 85; GND 84*)
6. How is pure HBr prepared? How does it differ from HF, HCl and HI? (*Calicut 86*)
7. Explain the following :
   (*i*) HF is a liquid (b.pt. = 19°C) while HCl is a gas.
   (*ii*) HBr cannot be prepared by the action of conc. H_2SO_4 on a bromide salt. (*Kanpur 2000*)
8. Explain why, in aqueous solution, HF behaves as a weak acid in comparison to other hydrogen acids. (*Avadh 2000*)
9. Give IUPAC names of HClO, $HClO_2$, $HClO_3$ and $HClO_4$. (*Lucknow 2001*)

CHAPTER

40

Binary Halogen-Oxygen Compounds and Oxyacids of Halogens

Binary Halogen-Oxygen Compounds

Halogens do not combine directly with oxygen. However, binary halogen-oxygen compounds have been prepared by indirect methods. The known compounds of this type are : (oxidation number of halogen atom is given in bracket) $OF_2(-1)$, $O_2F_2(-1)$; $Cl_2O(+1)$, $ClO_2(+4)$, ClO_3 or $Cl_2O_6(+6)$, $Cl_2O_7(+7)$; $Br_2O(+1)$, BrO_2 (+ 4), $BrO_3(+6)$; I_2O_4 (+ 4), I_2O_5 (+ 5), I_4O_9 or $I^{3+}[I^{5+}O_3]_3$. Since F is more electronegative than oxygen, fluorine-oxygen compounds are called *fluorides of oxygen* rather than the oxides of fluorine, *e.g.* OF_2 is called *oxygen difluoride* and not *difluorine oxide*. Similarly O_2F_2 is called *dioxygen difluoride* and not difluorine dioxide. On the other hand, since oxygen is more electronegative than Cl, Br and I, oxygen compounds with these halogens are called the oxides of these halogens rather than the halides of oxygen, *e.g.* ClO_2 is called *chlorine dioxide* rather than dioxygen chlorine.

Fluorides of Oxygen

1. Oxygen Difluoride, OF_2.

It is prepared by passing F_2 through 2% NaOH solution.

$$2NaOH + 2F_2 \longrightarrow OF_2 + 2NaF + H_2O$$

The gas obtained by this method is collected over water. It is a pale yellow poisonous gas (b.pt. = –145°C, m.pt. = –223.8°C). It is very slightly soluble in water. It is a stable gas. It is relatively unreactive and can be mixed with H_2, CH_4 or CO without reaction although explosion will take place on sparking. It forms an explosive mixture with Cl_2, Br_2 and I_2. It dissociates into its elements on heating. It reacts slowly with H_2O but explodes with steam.

$$OF_2 + H_2O \longrightarrow O_2 + 2HF$$

It is readily hydrolysed by base. It is powerful oxidising agent. For example it liberates I_2 from KI solution

$$OF_2 + 2OH^- \longrightarrow O_2 + 2F^- + H_2O$$

$$OF_2 + 4KI + H_2O \longrightarrow 2KF + 2KOH + I_2$$

Metals and non-metals are oxidised and/or fluorinated by it. Xenon reacts with it in an electric discharge to form a mixture of fluoride and oxy-fluoride.

2. Dioxygen Difluoride, O_2F_2.

It is prepared by passing an electric discharge through a mixture of F_2 and O_2 cooled to about –185°C. It is a solid (m.pt. = –163.5°). On increasing the temperature O_2F_2 is converted into a pale-brown gas. Above –100°C, O_2F_2 is decomposed into F_2 and O_2. It is extremely potent fluorinating and oxidising agent. Many substances explode on exposure at low temperatures and even C_2F_4 is changed into COF_2, CF_4 etc. With Cl_2, O_2F_2 gives a purple and fairly stable intermediate compound, $(O_2ClF_2)_n$. O_2F_2 is used for oxidising primary aliphatic amines to the corresponding nitroso compounds.

Oxides of Chlorine

1. Chlorine Monoxide, Cl_2O

It is prepared by passing dry Cl_2 over freshly precipitated yellow mercuric oxide (HgO) previously heated to 300–400°C and contained in a cooled tube.

$$HgO + 2Cl_2 \text{ (dry)} \longrightarrow HgCl_2 + Cl_2O$$

It is a brownish-yellow gas which condenses in a freezing mixture to an orange coloured liquid (b.pt. = 2°C and m.pt. = –120.6°C). It has characteristic penetrating odour. Liquid Cl_2O explodes readily on heating or sparking giving Cl_2 and O_2. It also explodes when the sides of the test-tube containing it are scratched with a file or a glass rod.

$$2Cl_2O \longrightarrow 2Cl_2 + O_2$$

It dissolves in H_2O giving a golden yellow solution of hypochlorous acid, HClO.

$$Cl_2O + H_2O \rightleftharpoons 2HClO$$

It is, therefore, known as *anhydride of hypochlorous acid.* On cooling the aqueous solution of Cl_2O strongly, crystalline hydrate, $Cl_2O.H_2O$ (m.pt. = –36°C) is obtained. It is a strong oxidising agent and oxidises HCl to Cl_2.

$$Cl_2O + 2HCl \longrightarrow 2Cl_2 + H_2O$$

It attacks mercury but only slowly.

The structure of Cl_2O molecule is the same as that of H_2O molecule. Thus Cl_2O molecule has V-shape (or angular or bent shape) as shown in Fig. 40.1 given in the margin. This shape results from sp^3 hybridisation of Cl atom. Since the electronegativity value of Cl atom is less than that of O-atom, the electron pairs used in the formation of O—Cl bonds in the molecule are nearer to O-atom and also at the same time (*lp*—*lp*) repulsion becomes less than (*bp*—*bp*) repulsion. Hence ClOCl bond angle increases from the expected tetrahedral angle to 111°.

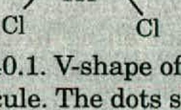


Fig. 40.1. V-shape of Cl_2O molecule. The dots shown at O-atom indicate the lone pairs of electrons.

2. Chlorine Dioxide, ClO_2

Preparation. Pure ClO_2 is obtained by passing dry Cl_2 over $AgClO_3$ heated to 90°C.

$$2AgClO_3 + Cl_2 \text{ (dry)} \longrightarrow 2AgCl + 2ClO_2 + O_2$$

The resulting gaseous mixture is passed through a freezing mixture when Cl_2 condenses while ClO_2 passes on condensation.

Properties. It is a dark yellow pungent smelling gas which can be condensed to a dark red liquid (b.pt. = 11°C). This liquid freezes at –9°C to an orange red crystalline solid. The liquid and solid both are fairly stable in dark but are slowly decomposed when exposed to light. The gas explodes and is decomposed into Cl_2 and O_2 by an electric spark, on heating with a glass rod or hot wire and in contact with turpentine, alcohol or ether

$$2ClO_2 \longrightarrow Cl_2 + 2O_2$$

It dissolves in H_2O giving a mixture of chlorous ($HClO_2$) and chloric acids ($HClO_3$).

$$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$$

With alkalies it gives a mixture of chlorite and chlorate (*e.g.* $KClO_2$ and $KClO_3$ with KOH)

$$2ClO_2 + 2KOH \longrightarrow KClO_2 + KClO_3 + H_2O$$

It is a powerful oxidising and bleaching agent. It liberates I_2 from acidified KI solution. Phosphorus, sulphur and many organic substances spontaneously catch fire in the gas. Like Cl_2O, ClO_2 also reacts with Hg but slowly. With O_3 at 0°C, it gives Cl_2O_6.

$$2ClO_2 + 2O_3 \longrightarrow Cl_2O_6 + 2O_2$$

Uses. It is used (*i*) for bleaching the highest grade paper pulp (*ii*) in water purification and for odour control. (*iii*) for improving the quality of low-grade fats and oils. (*iv*) in making the wool unshrinkable.

Structure. ClO_2 molecule has one coordinate, one three- electron and one two-electron (normal covalent) bond. Due to the presence of three-electron bond, ClO_2 is an odd-electron molecule. The presence of one unpaired electron in three-electron bond explains the paramagnetic character, colour and reactivity of the molecule.

Like NO_2 molecule, ClO_2 molecule also has a symmetrical angular (or bent or V) shape [Fig. 40.2(*a*)]. Each of the Cl–O bond distane is equal to 1.49A° and OClO bond angle to 118°. Cl–O bond length (= 1.49A°) is shorter than the single Cl–O bond length which is equal to the sum, $r(Cl) + r(O) = 0.99 + 0.73 = 1.72A°$. The shortening in the bond length is due to the presence of the three-electron bond in the molecule.

Here it should be noted that, unlike NO_2, ClO_2 has no tendency to dimerise. This is perhaps due to the fact the unpaired electron present in the three-electron bond is less localised on the central chlorine atom than in other odd-electron molecules. According to another view, ClO_2 molecule has the structure shown in Fig. 40.2 (*b*). This structure arises from sp^3 hybridisation of Cl-atom.

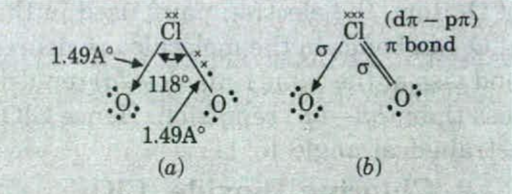


Fig. 40.2. Structure of ClO_2 molecule (*a*) Angular shape of ClO_2 molecule. (*b*) Structure of ClO_2 molecule based on sp^3 hybridisation of Cl-atom.

3. Dichlorine Hexoxide, $Cl_2O_6 \rightleftharpoons 2ClO_3$

It is best prepared by the action of O_3 on ClO_2 at 0°C atom.

$$2ClO_2 + 2O_3 \longrightarrow Cl_2O_6 + 2O_2$$

It is a dark red liquid (density = 1.65) which melts at 35°C. It is an explosive liquid, but less so than Cl_2. It is unstable and decomposes into ClO_2 and O_2 even at its melting point. It reacts violently with cooled water vapours and produces perchloric acid monohydrate ($HClO_4.H_2O$) or oxomium perchlorate, $(H_3O^+)\,(ClO_4^-)$ and chloric acid, $HClO_3$.

$$Cl_2O_6 + 2H_2O \longrightarrow HClO_4.H_2O \text{ or } (H_3O^+)\,(ClO_4^-) + HClO_3$$

With an alkali, it gives perchlorate and chlorate.

$$Cl_2O_6 + 2NaOH \longrightarrow NaClO_4 + NaClO_3 + H_2O$$

With HF, it gives $HClO_4$ and chloryl fluoride, ClO_2F.

$$Cl_2O_6 + HF \longrightarrow HClO_4 + ClO_2F$$

In the vapour (gaseous) state it exists principally as ClO_3 molecule which has odd number of electrons (= $7 + 6 \times 3 = 25$) and hence paramagnetic while in the liquid state it gets dimerised and exists as Cl_2O_6 which has even number of electrons (= $7 \times 2 + 6 \times 6 = 50$) and hence is diamagnetic.

$$\underset{\text{liquid}}{Cl_2O_6} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftarrows}} \underset{\text{vapour}}{2ClO_3}$$

The structure of Cl_2O_6 is unknown.

4. Chlorine Heptoxide, Cl_2O_7. Preparation. It is prepared by the dehydration of anhydrous $HClO_4$ with P_2O_5 at –10°C followed by vacuum distillation with precautions against explosions.

$$2HClO_4 + P_2O_5 \longrightarrow Cl_2O_7 + 2HPO_3.$$

Properties. It is a colourless oily liquid (b.pt. = 82°C) which is extremely explosive in nature. It is more stable than Cl_2O or ClO_2 and may be poured on phosphorus, sulphur, wood or paper without explosion. It explodes on heating or on percussion in a few days. It slowly reacts with H_2O forming $HClO_4$. Thus Cl_2O_7 is the anhydride of perchloric.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

Structure. Infra red spectrum of Cl_2O_7 in vapour state has shown that this molecule has two ClO_3 groups which are linked together by an O-atom, *i.e.* Cl_2O_7 molecule has the structure, $O_3Cl—O—ClO_3$ in which two tetrahedra are sharing one O-atom (See Fig. 40.3). The molecule is polar ($\mu = 0.72$).

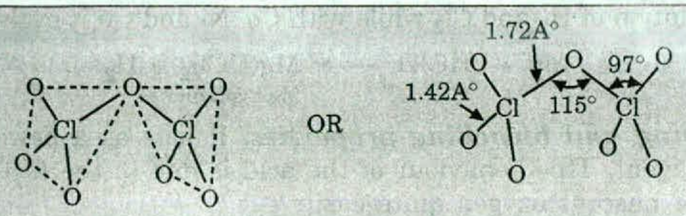


Fig. 40.3. Structure of Cl_2O_7 molecule.

Oxy-acids of Halogens

Except fluorine, all the remaining halogens form oxy-acids, which are grouped into four classes namely (1) *Hypo halous acids*, HXO(+ 1), *e.g.* hypochlorous acid (HClO), hypobromous acid (HBrO), hypoiodous acid (HIO) (2) *Halous acids*, HXO_2(+ 3), *e.g.* chlorous acid ($HClO_2$) (3) *Halic acids*, HXO_3(+ 5), *e.g.* chloric acid ($HClO_3$), bromic acid ($HBrO_3$), iodic acid (HIO_3) (4) *Perhalic acids*, HXO_4 (+ 7) *e.g.* perchloric acid ($HClO_4$), perbromic acid ($HBrO_4$), periodic acid (HIO_4). The numbers given in brackets indicate the oxidation state of the halogen atom in the acid. Here we shall discuss the oxy-acids of chloride and their important salts only.

Oxy Acids of Chlorine

I. Hypochlorous Acid, HClO

Preparation. This acid is known only in solution. It is best prepared by shaking chlorine water with freshly precipitated yellow mercuric oxide, HgO

$$2Cl_2 + 2HgO + H_2O \longrightarrow \underset{\substack{\text{Oxy chloride}\\ \text{of mercury}\\ \text{(insoluble)}}}{Hg_2OCl_2} + 2HClO$$

Commercially it is prepared by passing CO_2 into a suspension of bleaching powder, $CaOCl_2$ in water and then distilling.

$$2CaOCl_2 + CO_2 + H_2O \longrightarrow CaCl_2 + CaCO_3 + 2HOCl$$

Properties. (*i*) **Physical state and colour :** The concentrated solution of the acid is yellow in colour while the dilute solution is colourless. It is a weak acid, even weaker than H_2CO_3. Its dissociation constant value is equal to 3×10^{-8} at 20°C.

(ii) Decomposition. The dilute solution of the acid is fairly stable in the dark while concentrated solution is unstable and hence decomposes into HCl and O_2

$$2HClO \longrightarrow 2HCl + O_2$$

The decomposition is accelerated by platinum black, manganese oxide and cobalt oxide.

On distillation, HClO decomposes into H_2O and Cl_2O.

$$2HClO \xrightarrow{\text{Distillation}} Cl_2O + H_2O$$

(iii) Action on metals. HClO dissolves Mg with the evolution of H_2; Fe and Al with the evolution of H_2 and Cl_2 while with Co, Ni and Cu it evolves Cl_2 and O_2.

$$Mg + 2HClO \longrightarrow \underset{\text{Mg.hypochlorite}}{Mg(OCl)_2} + H_2$$

(iv) Oxidising and bleaching properties. It acts as a powerful oxidising and bleaching agent. This behaviour of the acid is due to the fact that the acid can liberate the nascent oxygen quite easily.

$$HClO \longrightarrow HCl + O$$

Thus the acid liberates I_2 from the acidified KI solution, oxidises $Cr(OH)_3$ to chromate (CrO_4^{2-}) in alkaline medium and oxidises white $Mn(OH)_2$ to brown hydrated maganic oxide, $MnO_2.2H_2O$ or $Mn(OH)_4$.

$$2KI + HClO + HCl \longrightarrow 2KCl + H_2O + I_2$$

$$2Cr(OH)_3 + 3NaClO + 4NaOH \longrightarrow 2Na_2CrO_4 + 3NaCl + 5H_2O$$

$$Mn(OH)_2 + NaOCl + H_2O \longrightarrow MnO_2.2H_2O + \text{ or } Mn(OH)_4 + NaCl.$$

(v) Action of H_2O_2. The acid reacts with H_2O_2 to give O_2.

$$HClO + H_2O_2 \longrightarrow HCl + H_2O + O_2$$

(vi) Action on metallic mercury. When the acid is shaken with metallic mercury, a light brown precipitate of basic mercuric chloride, HgCl(OH) which is soluble in HCl is obtained.

$$2Hg + 2HClO \longrightarrow \underset{\substack{\text{Basic}\\ \text{mercuric}\\ \text{chloride}}}{2HgCl(OH)}$$

(vii)Action of alkalies. With alkalies it forms salts which are called *hypochlorites.*

Uses. The acid is used for bleaching paper pulp etc.

Structure of hypochlorite ion, ClO^-. ClO^- ion has linear shape (Fig. 40.4) with Cl—O bond distance = 1.70A° and Cl—O bond energy is equal to 209 KJ/mole. Linear shape results from sp^3 hybridisation of Cl atom (central atom).

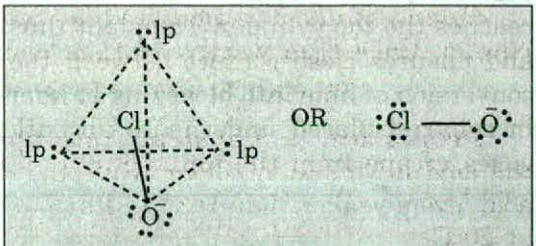


Fig. 40.4. Linear shape of hypochlorite ion, ClO^-.

Bleaching Powder, $CaOCl_2$ or Ca(OCl)Cl (Mixture of salts of HCl and HClO)

Bleaching powder is probably not a single compound but is a mixture of salts of hydrochloric acid (HCl) and hypochlorous acid (HClO) and hence has the formula $Ca^{2+}Cl^-(ClO)^-$ or $CaOCl_2$. The formula, CaCl(ClO)shows that bleaching powder is calcium *chloro-hypochlorite.* The formula *viz.* $CaOCl_2$ explains all the properties of bleaching powder.

Manufacture. Bleaching powder is manufactured by the action of Cl_2 on dry slaked lime, $Ca(OH)_2$. Following are the two main views regarding the formation of bleaching powder by this method :

(i) Odling's view (1861). According to this view, bleaching powder is calcium chloro-hypochlorite, $Ca^{2+}Cl^-(ClO)^-$.

$$Ca(OH)_2 + Cl_2 \longrightarrow \underset{\substack{\text{Calcium chloro-}\\ \text{hypochlorite}\\ \text{(Bleaching}\\ \text{powder)}}}{CaCl(ClO)} + H_2O$$

(ii) Bunn, Clark and Clifford's view (1935). According to this view, bleaching powder is usually supposed to be a mixture of calcium hypochlorite, $Ca(OCl)_2$ and basic calcium chloride, $CaCl_2.Ca(OH)_2.\ H_2O$.

Thus the formation of bleaching powder can be shown as :

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow \underset{\text{Cal . hypo-chlorite}}{Ca(OCl)_2} + CaCl_2 + 2H_2O$$

$$CaCl_2 + Ca(OH)_2 + H_2O \longrightarrow \underset{\text{Basic calcium chloride}}{CaCl_2 . Ca(OH)_2 . H_2O}$$

$$\text{On adding : } 3Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{Ca(OCl)_2 + CaCl_2 . Ca(OH)_2 . H_2O}_{\text{Bleaching powder}} + H_2O$$

The chlorine used in the manufacture of bleaching powder should be dilute and the temperature should be maintained below 40°C.

The manufacture of bleaching powder is carried in any of the following two plants :

1. Hasenclever's plant (*Old method*). The Hasenclever's plant used for the manufacture, consists of a number of horizontal cast iron cylinders each containing a rotating shaft, fitted with blades. Slaked lime is fed in at the hopper and is pushed from one end of the cylinder to the other with the help of the blades when the shaft rotates. A stream of chlorine is introduced from near the bottom (*See* Fig. 40.5) in the opposite direction and it is completely absorbed by the time it reaches the top cylinder. The plant thus works on the *principle of counter-current* and ensures close contact between the slaked lime and Cl_2 and thus complete conversion of lime into bleaching powder takes place. Bleaching powder is collected in a barrel placed underneath an outlet in lowermost cylinder while the waste gases escape from the top.

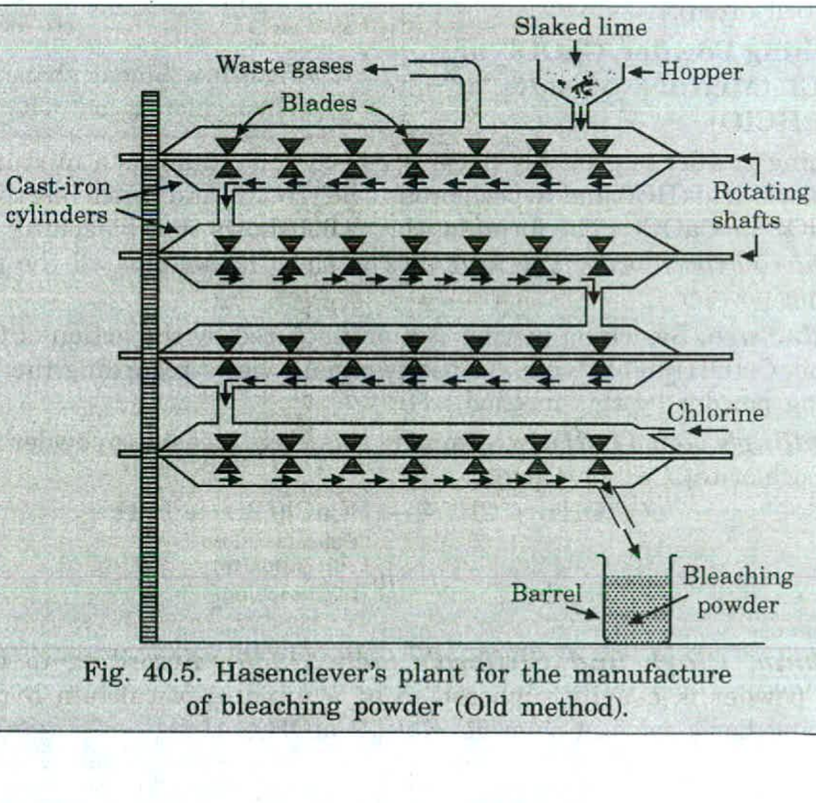


Fig. 40.5. Hasenclever's plant for the manufacture of bleaching powder (Old method).

2. Bachmann's plant (*Modern method*). Now-a-days bleaching powder is prepared in Bachmann's plant (*See* Fig. 40.6). It consists of a vertical cast iron tower fitted with eight shelves at different heights each equipped with rotating rakes.

Slaked lime is conveyed to the top of the tower with the help of a suitable air pumping arrangement and fed into the tower through a hopper at the top. A current of chlorine is introduced at the seventh shelf. The slaked lime thus added moves downward with the help of rotating rakes and meets an upcoming current of Cl_2. Slaked lime and Cl_2 react together and form bleaching powder which is collected in a barrel placed at the base. A current of hot air is blown into the eighth shelf to remove the uncombined free chlorine. This uncombined free chlorine goes out of the exit at the top.

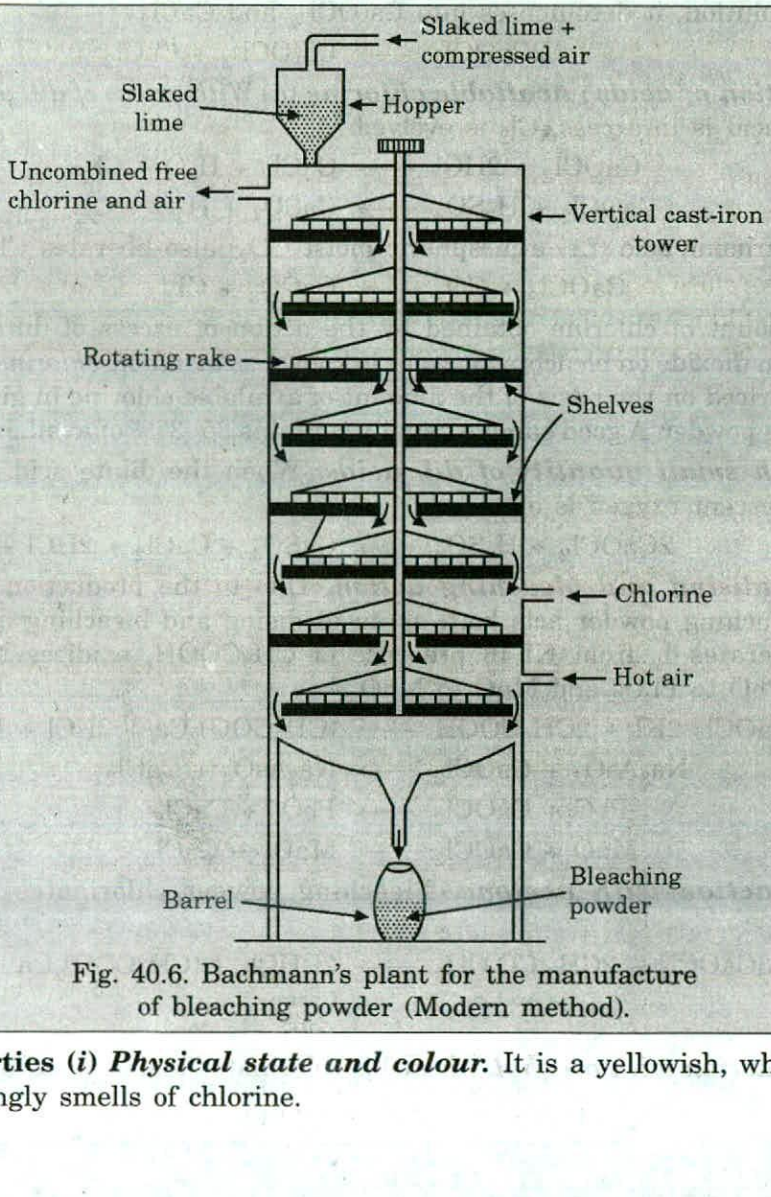


Fig. 40.6. Bachmann's plant for the manufacture of bleaching powder (Modern method).

Properties (*i*) *Physical state and colour.* It is a yellowish, white powder which strongly smells of chlorine.

(ii) Solubility in water. It is soluble in H_2O but a clear solution is never obtained due to the presence of impurities of lime in it.

With H_2O, it gives $Ca(OCl)_2$ which, on decomposition, gives O_2.

$$2CaOCl_2 + H_2O \longrightarrow CaCl_2 + Ca(OCl)_2 + H_2O$$
$$Ca(OCl)_2 \longrightarrow CaCl_2 + O_2$$

(iii) Decomposition. (*a*) On long standing, it slowly decomposes into a mixture of $Ca(ClO_3)_2$ and $CaCl_2$ (*Auto-oxidation*).

$$6CaOCl_2 \longrightarrow Ca(ClO_3)_2 + 5CaCl_2$$

(*b*) In presence of $CoCl_2$ (catalyst), it loses its oxygen.

$$6CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2 + O_2$$

(*c*) In solution, it decomposes into $Ca(OCl)_2$ and $CaCl_2$

$$2CaOCl_2 \longrightarrow Ca(OCl)_2 + CaCl_2$$

(iv) Action of acids : Available chlorine (*a*) *With excess of dil. acids.* When the dilute acid is in *excess*, Cl_2 is evolved.

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$
$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

Even carbonic acid (*i.e.* atmospheric moist CO_2) also liberates Cl_2

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

The amount of chlorine obtained by the action of excess of dilute acids or moist carbon dioxide on bleaching powder is known as *available chlorine*. Bleaching powder is priced on the basis of the amount of available chlorine in given sample of bleaching powder. A good sample usually contains 35–37% of available chlorine.

(b) With small quantity of dil. acids. When the dilute acid is in small quantity, nascent oxygen is obtained.

$$2CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + CaCl_2 + 2HCl + 2O$$

(v) Oxidising and bleaching action. Due to the production of nescent oxygen, bleaching powder acts both as an oxidising and bleaching agent. Thus $CaOCl_2$ liberates I_2 from KI in presence of CH_3COOH, oxidises Na_3AsO_3 to Na_3AsO_4, PbO to PbO_2 and MnO to MnO_2.

$$CaOCl_2\ 2KI + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + 2KCl + H_2O + I_2$$
$$Na_3AsO_3 + CaOCl_2 \longrightarrow Na_3AsO_4 + CaCl_2$$
$$PbO + CaOCl_2 \longrightarrow PbO_2 + CaCl_2$$
$$MnO + CaOCl_2 \longrightarrow MnO_2 + CaCl_2$$

(vi) Reaction with acetone. Bleaching powder chlorinates acetone to chloroform.

$$3CaOCl_2 + \underset{\text{Acetone}}{2CH_3.CO.CH_3} \longrightarrow \underset{\text{Chloro-form}}{2CHCl_3} + (CH_3COO)_2Ca + 2Ca(OH)_2$$

(vii)Reaction with alcohol. Alcohol is chlorinated and oxidised by bleaching powder

$$4CaOCl_2 + 2C_2H_5OH \longrightarrow 2CHCl_3 + (HCOO)_2Ca + Ca(OH)_2 + 2H_2O + CaCl_2$$

(viii) Action of NH_4OH. When bleaching powder is heated with NH_4OH, N_2 gas is liberated

$$3CaOCl_2 + 2NH_4OH \longrightarrow CaCl_2 + 5H_2O + N_2$$

Uses. It is used *(i)* For bleaching cotton, linen and wood pulp in textile and paper factories. Delicate articles like straw or silk are not bleached by bleaching powder as these are injured by it. *(ii)* As a disinfectant and germicide for sewers and drains and for sterilization of water. *(iii)* For making wool unshrinkable. *(iv)* In the manufacture of chloroform. *(v)* As an oxidising agent in industry. *(vi)* For removing poisonous gases from the atmosphere during the war time.

Constitution of bleaching powder

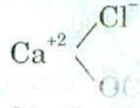
Following different views have been put forward to explain the constitution of bleaching powder.

1. Dalton's view. Dalton in 1813 suggested that bleaching powder is a loose combination of quick lime (CaO) and chlorine (Cl_2). But this view was rejected because of the fact that quick lime has no tendency to absorb Cl_2.

2. Balard's view. In 1835 Balard suggested that bleaching powder is an equimolecular mixture of calcium chloride ($CaCl_2$) and calcium hypochlorite [$Ca(OCl)_2$]. Thus according to this view bleaching powder has the mixed formula, $CaCl_2.Ca(OCl)_2$. If this formula is supposed to be true, bleaching powder should exhibit the properties of both $CaCl_2$ and $Ca(OCl)_2$. But, in fact, bleaching powder does not possess the properties of both the salts as indicated by the facts : *(a)* $CaCl_2$ is extremely daliquescent while bleaching powder is not so. *(b)* $CaCl_2$ is soluble in alcohol while bleaching powder is not soluble. *(c)* Moist CO_2 or dil. acid has no action on $CaCl_2$ while they liberate the whole of the available chlorine from bleaching powder.

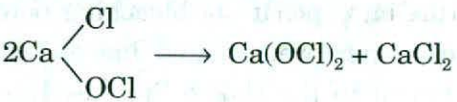
$$CaCl_2 + CO_2 \longrightarrow \text{No reaction}$$
$$\text{Bleaching powder} + CO_2 \longrightarrow CaCO_3 + Cl_2$$

(d) Bleaching powder cannot be obtained by mixing $CaCl_2$ and $Ca(OCl)_2$ in equimolecular proportions. These points show that bleaching powder cannot be regarded as a mixture of $CaCl_2$ and $Ca(OCl)_2$.

3. Odling's view. In 1861, Odling suggested that bleaching powder is a mixed salt of HCl and HClO and hence gave the formula, CaCl(OCl) or  $Ca^{+2}\left\langle\begin{matrix}Cl^- \\ OCl^-\end{matrix}\right.$

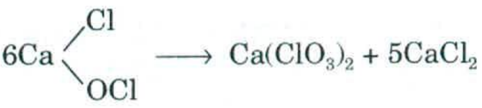
Thus according to this view bleaching powder is *calcium chloro-hypochlorite*. The formula explains all the properties of bleaching powder. For example :

(a) In solution bleaching powder decomposes into $Ca(OCl)_2$ and $CaCl_2$.



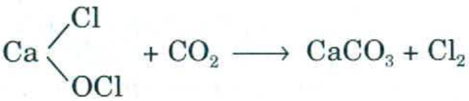
$$2Ca\left\langle\begin{matrix}Cl \\ OCl\end{matrix}\right. \longrightarrow Ca(OCl)_2 + CaCl_2$$

(b) On long standing, bleaching powder undergoes auto- oxidation into $Ca(ClO_3)_2$ and $CaCl_2$.



$$6Ca(Cl)(OCl) \longrightarrow Ca(ClO_3)_2 + 5CaCl_2$$

(*c*) The action of dil. acids or moist CO_2 on bleaching powder gives all the available chlorine.



$$Ca(Cl)(OCl) + CO_2 \longrightarrow CaCO_3 + Cl_2$$

4. Bunn, Clark and Clifford's view. In 1935, these chemists suggested that when Cl_2 gas is passed over dry slaked lime [$Ca(OH)_2$], basic calcium hypochiorite, $Ca(ClO)_2.2Ca(OH)_2$ and non-deliquescent basic calcium chloride, $CaCl_2.Ca(OH)_2.H_2O$ are obtained.

$$\underset{\text{Slaked lime}}{5Ca(OH)_2} + 2Cl_2 \longrightarrow \underset{\text{Basic calcium hypochlorite}}{Ca(ClO)_2.2Ca(OH)_2} + \underset{\text{Basic cal. chloride}}{CaCl_2.Ca(OH)_2.H_2O} + H_2O$$

Basic calcium hypochlorite, $Ca(ClO)_2.\ 2Ca(OH)_2$ on further chlorination gives calcium hypochlorite, $Ca(ClO)_2.4H_2O$. Hence according to this view bleaching powder is a *mixture of calcium hypochlorite*, $Ca(ClO)_2.4H_2O$ and *basic calcium choride*, $CaCl_2.Ca(OH)_2.\ H_2O$. This view is in full agreement with the physical and chemical properties of bleaching powder and is confirmed by phase rule study, and microscopic and X-ray analysis.

Available Chlorine in Bleaching Powder

The amount of chlorine obtained by the action of excess of dilute acids or carbon dioxide on bleaching powder is known as available chlorine. Calculated on the basis of Odling formula, the maximum percentage of available chlorine from bleaching powder is about 49%.

$$\underset{\substack{40\,+\,16\,+\,71\,+\,18\\=\,145}}{CaOCl_2.H_2O} + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O + \underset{\substack{35.5\,\times\,2\\=\,71}}{Cl_2}$$

145 gm. of $CaOCl_2.H_2O$ contains chlorine = 71 gm.

$$1 \;\text{,,}\quad \text{,,}\quad \text{,,}\quad \text{,,} \qquad = \frac{71}{145}\ \text{gm.}$$

$$100 \;\text{,,}\quad \text{,,}\quad \text{,,}\quad \text{,,} \qquad = \frac{71 \times 100}{145} = 49$$

i.e., Percentage of available chlorine = 49%.

The actual percentage of available chlorine in the commercial sample of bleaching powder has, however, been found to be much lower. It is nearly 35–40%. The low percentage is due to :

(*i*) Loss of chlorine on exposure of bleaching powder to air.

(*ii*) Incomplete reaction between slaked lime and chlorine during it formation.

(*iii*) Impurities present in the slaked lime used for the manufacture.

Estimation of Available Chlorine in Bleaching Powder

The amount of available chlorine in bleaching powder can be estimated by two methods :

(*i*) **Arsenite method** (*Pento's method*). Chlorine can oxidise sodium arsenite to sodium arsenate. Thus the amount of sodium arsenite oxidised to sodium arsenate by given weight of bleaching powder sample is a measure of the available chlorine present in it.

$$Na_3AsO_3 + CaOCl_2 \longrightarrow Na_3AsO_4 + CaCl_2$$

A standard solution of sodium arsenite is prepared. A weighed quantity of bleaching powder is suspended in distilled water. A known volume of standard arsenite solution is then added to this suspension. A part of sodium arsenite is oxidised to sodium arsenate by the available chlorine. Tile unused sodium arsenite solution is estimated volumetrically by titration against a standard iodine solution in the presence of sodium bicarbonate and using starch solution as an indicator. The percentage of available chlorine can be calcualated from the volume of sodium arsenite used. Finally the amount of available chlorine in the sample of bleaching powder is calculated with the help of the following relationship :

1 ml. of $Na_3AsO_3 \equiv 0.0354$ g. of available chlorine.

(*ii*) **Iodometric method** (*Bunsen and Wagner's method*). It consists in treating a suspension of bleaching powder in distilled water with an excess of potassium iodide and acetic acid. Available chlorine in bleaching powder libarates an equivalent quantity of iodine from potassium iodide.

$$CaOCl_2 + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + Cl_2 + H_2O$$

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

Iodine thus liberated is estimated by titrating against a standard (N/10) sodium thiosulphate solution using starch solution as an indicator.

$$\underset{\text{Sod. thiosulphate}}{2Na_2S_2O_3} + I_2 \longrightarrow \underset{\text{Sod. tetrathionate}}{Na_2S_4O_6} + 2NaI$$

1 ml. of N/10 $Na_2S_2O_3 \equiv 0.00355$ g. of available chlorine

II. Chlorous Acid, $HClO_2$

It is the only definitely known halous acid. Being a weak acid, it cannot be isolated in the free state. In aqueous solution it is obtained by treating a suspension of barium chlorite, $Ba(ClO_2)_2$ with dil. H_2SO_4 and filtering off the precipitate of $BaSO_4$.

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow 2HClO_2 + \underset{\text{ppt.}}{BaSO_4}$$

The freshly prepared solution of the acid is colourless but it soon decomposes to ClO_2 which colours the solution yellow. The acid gives a violet colour with ferrous sulphate. The acid undergoes auto-oxidation at ordinary temperature and changes into a mixture of hypochlorous acid (HClO) and chloric acid ($HClO_3$).

$$2HClO_2 \longrightarrow HClO + HClO_3$$

The acid liberates I_2 from an iodide.

$$4KI + HClO_2 + H_2O \longrightarrow 4KOH + HCl + 2I_2$$

Chlorite ion, ClO_2^- has *angular shape* (Fig 40.7) which results from sp^3 hybridisation of Cl atom (central atom). Each Cl—O bond distance is equal to 1.64A° and each OClO bond angle is equal to 111°.Cl—O bond energy is equal to 245 KJ/mole.

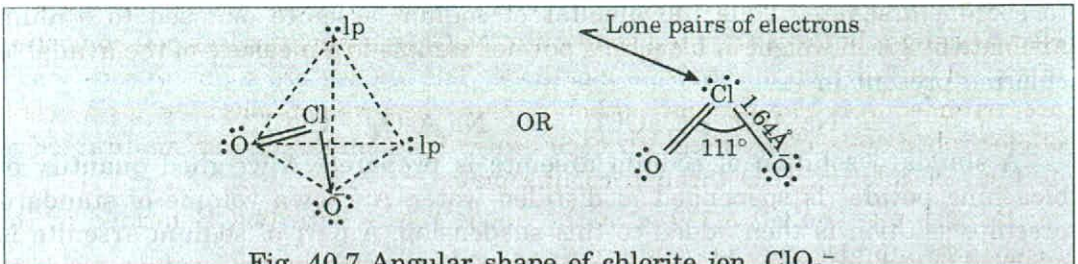


Fig. 40.7 Angular shape of chlorite ion, ClO_2^-

III. Chloric Acid, $HClO_3$

This acid is known only in solution. The acid is conveniently prepared by the action of dil. H_2SO_4 on barium chlorate, $Ba(ClO_3)_2$.

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow \underset{\text{Insoluble}}{BaSO_4} + 2HClO_3$$

Insoluble $BaSO_4$ is filtered off and the excess (*i.e.* unused) of H_2SO_4 is precipitated with baryta water. The filtrate is evaporated in a vacuum desicater over conc. H_2SO_4 until it contains 40% $HClO_3$. Note that on further concentration, the acid decomposes and hence further concentration is not required.

$$3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$$

Concentrated acid is colourless and pungent smelling liquid. It is fairly stable in the dark. When exposed to light, it decomposes and gives O_2. It is for this reason that in the light, it acts as a powerful oxidising and bleaching agent. Organic substances like paper, cotton, wool etc. catch fire in contact with the acid. On evaporation or distillation, the acid undergoes disproportionation to give perchloric acid ($HClO_4$) and ClO_2.

$$\underset{\text{(O.N. of Cl = + 5)}}{3HClO_3} \longrightarrow \underset{\text{(O.N. of Cl = + 7)}}{HClO_4} + \underset{\text{(O.N. of Cl = + 4)}}{2ClO_2} + H_2O$$

Chlorate ion, ClO_3^- has trigonal pyramidal shape (Fig. 40.8) which results from sp^3 hybridisation of Cl atom. Two neutral O-atoms are linked with Cl-atom by double bonds while the negatively-charged O-atom is attached by a single bond. Each Cl–O bond distance is equal to 1.57 Å and each OClO bond angle has been found to be equal to 106°. Cl—O bond energy is equal to 244 KJ/mole.

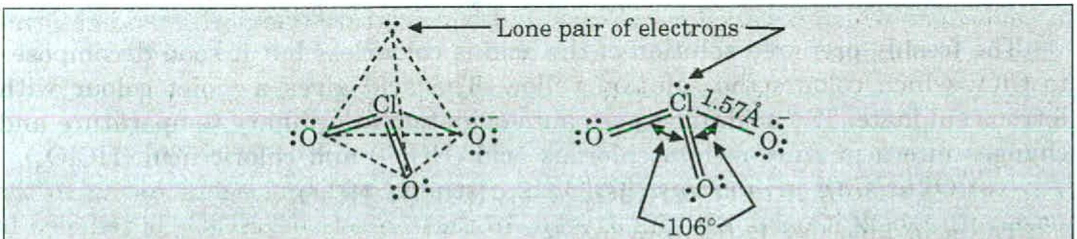


Fig. 40.8. Trigonal pyramidal shape of chlorate ion, ClO_3^-.

Potassium Chlorate, $KClO_3$ (Salt of $HClO_3$)

Preparation : It is an important salt of chloric acid, $HClO_2$ and *in the laboratory* it is prepared as :

$$6KOH \text{ (hot concentration solution)} + 3Cl_2 \longrightarrow KClO_3 + 5KCl + 3H_2O$$

Commercially it is prepared by electrolytic process which consists of electrolysing a hot concentrated solution of NaCl in a partitionless cell consisting of a steel tank which also acts as a cathode. The anodes are graphite rods which are arranged very close to each other so that the products obtained as a result of electrolysis mix and react with each other. The temperature is maintained at 40°C by circulating H_2O through cooling pipe.

Reactions. The Cl_2 set free at the anode reacts with NaOH formed at the cathode to produce $NaClO_3$

Ionisation : $NaCl \longrightarrow Na^+ + Cl^-$; $H_2O \longrightarrow H^+ + OH^-$

At cathode : $Na^+ + OH^- \longrightarrow NaOH$

$H^+ + e^- \longrightarrow H$; $H + H \longrightarrow H_2$

At anode : $Cl^- - e^- \longrightarrow Cl$; $Cl + Cl \longrightarrow Cl_2$

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

$NaClO_3$ obtained as above is treated with an equivalent quantity of KCl to convert $NaClO_3$ into $KClO_3$ which is least soluble and hence crystallises out on cooling.

$$NaClO_3 + KCl \longrightarrow KClO_3 + NaCl$$

Electrolysis of KCl solution gives $KClO_3$ directly but, because it is sparingly soluble, it crystallises during the course of electrolysis and creates trouble. Hence it is best to use NaCl for electrolysis instead of KCl.

Properties. (*i*) *Physical state and solubility.* $KClO_3$ is a white crystalline solid with m.pt. = 370°C. It is sparingly soluble in cold water but more so in hot water.

(*ii*) *Decomposition.* On heating above 400°C, $KClO_8$ decomposes as :

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

(*iii*) *Action of conc.* *sulphuric acid.* When it is heated with concentrated sulphuric acid, long explosions occur due to the breaking up of the molecules of chlorine dioxide obtained during the reaction.

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

(*iv*) *Action of conc.* *hydrochloric acid.* With concentrated hydrochloric acid, a yellow gas which is called *euchlorine* and is a mixture of chlorine and chlorine dioxide is obtained.

$$2KClO_3 + 4HCl \longrightarrow 2KCl + 2H_2O + \underbrace{Cl_2 + 2ClO_2}_{\text{Euchlorine gas}}$$

(*v*) *Oxidising properties.* $KClO_3$ is a strong oxidising agent owing to the ease with which it parts with its oxygen. In these reactions, $KClO_3$ is reduced to KCl. Thus $KClO_3$ oxidises HCl to Cl_2.

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

(vi) Reaction with S, P or charcoal. With sulphur, phosphorus or charcoal, $KClO_3$ forms an explosive mixture.

(vii) Action of iodine. Iodine in presence of nitric acid converts it into potassium iodate (KIO_3).

$$2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$$

Uses. (*i*) Potassium chlorate is used in the manufacture of gunpowder, matches, fire works and photographic flash powders and is preferred over $NaClO_3$, since the latter is hydroscopic. (*ii*) It is a strong insecticide, and is used as an antiseptic, especially in sore throat. A very dilute solution of the salt is used as a gargle for sore throat. (*iii*) In the laboratory, it is employed in the preparation of oxygen and potassium perchlorate and as an oxidising agent.

IV. Perchloric Acid, $HClO_4$

It is the most stable oxy-acid of chlorine. *Anhydrous* perchloric acid is prepared by distillating potassium perchlorate, $KClO_4$ with 96–97.5% H_2SO_4 under 10–20 mm. pressure at 90–160°C.

$$KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$$

It is purified by distilling at 40–60°C under 60 mm. pressure.

An aqueous solution of the acid is prepared by treating $Ba(ClO_4)_2$ with calculated quantity of dil. H_2SO_4 and removing the insoluble $BaSO_4$ by filtration.

$$Ba(ClO_4)_2 + H_2SO_4 \longrightarrow 2HClO_4 + \underset{\text{Insoluble}}{BaSO_4}$$

Anhydrous $HClO_4$ is a colourless mobile, hygroscopic and oily liquid. It fumes strongly in moist air and dissolves in water with a hissing sound due to the liberation of much heat. It forms hydrates with 1, 2, 2.5, 3, 3.5 molecules of water of crystallisation. It is unstable and decomposes with explosion on heating and sometimes merely on standing for a few days even in the dark. Aqueous solution of the acid is quite stable and does not decompose and hence can be kept indefinitely. It is highly dangerous acid and produces severe wounds on the skin. It is a powerful oxidising agent and inflames paper and wood. On dehydration with P_2O_5, it gives Cl_2O_7.

$$2HClO_4 + P_2O_5 \longrightarrow Cl_2O_7 + 2HPO_3$$

It is not reduced by nascent hydrogen but is reduced to chloride by strong reducing agents like $SnCl_2$, $CrCl_2$ etc. The aqueous acid is used in analysis for estimating potassium gravimetrically.

Perchlorate ion, ClO_4^- has tetrahedral shape (Fig. 40.9) which results from sp^3 hybridisation of Cl atom. Each Cl—O bond distance is equal to 1.45 Å and each of the OClO bond angles is equal to the tetrahedral angle (= 109.5°). Cl—O bond energy is equal to 364 KJ/mole.

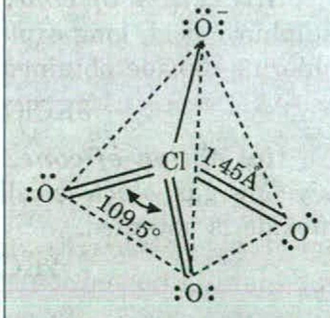


Fig. 46.9. Tetrahedral shape of perchlorate ion, ClO_4^-.

Potassium Perchlorate, $KClO_4$ (Salt of $HClO_4$)

It is the most important salt of perchloric acid. On *commercial scale*, it is prepared by electrolytic (anodic) oxidation of a conc. aqueous solution of $NaClO_3$ at room temperature. Sodium perchlorate, $NaClO_4$ thus formed is treated with KCl when sparingly soluble $KClO_4$ is precipitated. It is a colourless crystalline solid, sparingly soluble in water. On heating it decomposes as follows :

$$KClO_4 \xrightarrow{\Delta} KCl + 2O_2$$

With hot conc. H_2SO_4, it gives fumes of perchloric acid.

$$KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$$

It is used in fireworks and eplosives.

Conceptual Questions with Answers

Q.1 Write two uses of ClO_2.

Ans : (*i*) *ClO_2 is a powerful oxidising agent and chlorinating agent.* Large quantities of ClO_2 are used for bleaching wood pulp and cellulose and for purifying drinking water.

(*ii*) *It is an excellet bleaching agent.* Its bleaching powder is about 30 times higher than that of Cl_2 and is used for bleaching fluor or make write bread.

Q.2 Balance and complete the following redox reaction in basic reaction.

$$ClO_2 + SbO_2^- \longrightarrow ClO_2^- + Sb(OH)_6^-$$

Ans : The skeleton half-reactions can be written as :

$$\underset{(Sb = +3)}{SbO_2^-} \xrightarrow{\text{Oxidation}} \underset{(Sb = +5)}{Sb(OH)_6^-}$$

$$\underset{(Cl = +4)}{ClO_2} \xrightarrow{\text{Reduction}} \underset{(Cl = +3)}{ClO_2^-}$$

In the balanced form the above reactions can be written as :

$$SbO_2^- + 2H_2O + 2OH^- \xrightarrow{\text{Oxidation}} Sb(OH)_6^- + 2e^-$$

$$ClO_2 + e^- \xrightarrow{\text{Reduction}} ClO_2^- \,] \times 2$$

On adding : $SbO_2^- + 2H_2O + 2OH^- + 2ClO_2 \longrightarrow Sb(OH)_6^- + 2ClO_2^-$

Q.3 Discuss the structure of the following oxides (*i*) I_2O_4 (*ii*) I_4O_9 (*iii*) I_2O_5 (*iv*) Cl_2O_6

Ans : (*i*) **Structure of I_2O_4 molecule.** This molecule is believed to be the true oxide of iodine but is an ionic compound which is represented as $[IO]^+ [IO_3]^-$ and is called **iodosyl iodate.** In IO^+ ion I is in +3 oxidation state while in IO_3^- ion, I is in +5 oxidation state.

(*ii*) **Structure of I_4O_9 molecule.** This molecule is not believed to be a true oxide of iodine but is regarded as **iodine iodate,** $I^{+3}[IO_3]_3^-$ in which iodine is in +3 and +5 oxidation state.

(*iii*) **Structure of I_2O_5 molecule.** The infrared spectrum of I_2O_5 molecule indicates that this molecule has two IO_2 units which are joined together by O-atom. Thus I_2O_5 can be represented as $O_2I—O—IO_2$, *i.e.* I_2O_5 molecule has oxygen-bridged structure shown in Fig. 40.10. Each I-atom has *lp* of electrons. I-atom is sp^3 hybridised.

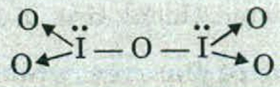


Fig. 40.10. Structure of I_2O_5 molecule

(*iv*) **Structure of Cl_2O_6 molecule.** The structure of Cl_2O_6 molecule is not known with certainty. However, its dissociation into two ClO_3 molecules shows that Cl_2O_6 is obtained by combining two ClO_3 molecules. Thus Cl_2O_6 molecule can be represented as $O_3Cl—ClO_3$ as shown in Fig. 40.11 Cl_2O_6 has one Cl—Cl bond which is formed by the sharing of two unpaired electrons on two Cl-atoms of two ClO_3 molecules. Thus in Cl_2O_6 molecule all the electrons are paired and hence this molecule is diamagnetic. Each Cl-atom is sp^3 hybridised. In this structure Cl-atom shows a covalency of seven.

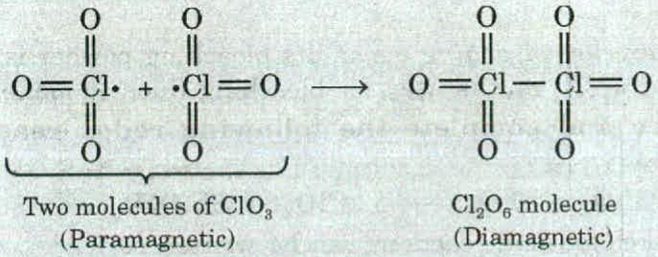
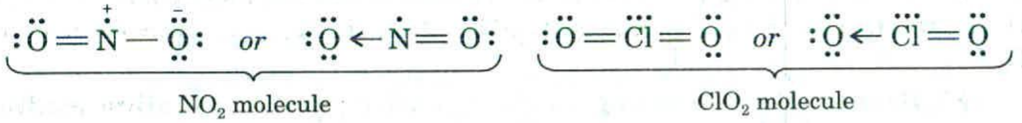


Fig. 40.11. Structure of Cl_2O_6 molecule

Q.4 Make a comparative study of NO_2 and ClO_2 molecules.

Ans. (*i*) The structures of the given molecules can be written as :



(*ii*) Both the molecules are odd electron molecules (NO_2 = 17, ClO_2 = 19)

(*iii*) N-atom in NO_2 molecule is sp^2 hybridised (σ-*bps* + *lps* $= 2 + \frac{1}{2} = 2\frac{1}{2}$), but in ClO_2 molecule Cl-atom is sp^3 hybridised (σ-*bps* + *lps* $= 2 + 1\frac{1}{2} = 3\frac{1}{2}$).

(*iv*) In both the molecules the central atom (*i.e.* N and Cl atoms) has one unpaired electron. Hence both the molecules are paramagnetic.

(*v*) On cooling, NO_2 dimerises to form N_2O_4 but ClO_2 does not dimerise.

(*vi*) NO_2 in the gaseous state has brown colour. ClO_2 also has marked colour.

(*vii*) NO_2 molecule has one $(p\pi–p\pi)\pi$ bond while ClO_2 molecule has one $(p\pi–d\pi)\pi$ bond.

(*viii*) NO_2 and ClO_2 both have angular geometry.

(*ix*) ONO bond angle = 132° and OClO bond angle = 118°.

(*x*) Both bond lengths in NO_2 = 120 pm and both bond lengths in ClO_2 = 149 pm.

(*xi*) B.O. in $NO_2 = \frac{2+1}{2} = 1.5$ but B.O. of $ClO_2 = 3.5$

Q.5 Name a compound of fluorine which shows +1 oxidation state. How is this compound prepared ? Is this a disproportionation reaction ?

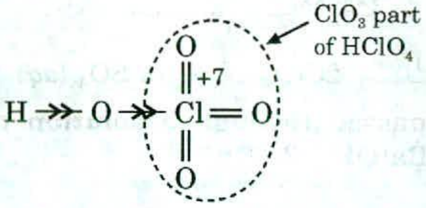
Ans. The compound of F which shows an oxidation state of +1 is HOF. It is prepared by passing F_2 over ice at 233 K.

$$\overset{0}{F}_2 + H_2O\,(ice) \xrightleftharpoons{233\text{ K}} HO\overset{+1}{F} + H\overset{-1}{F}$$

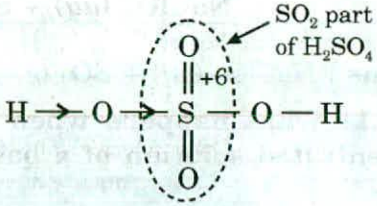
This is a disproportionation reaction since the oxidation state of F decreases from zero in F_2 to −1 in HF and increases to +1 in HOF.

Q.6 Perchloric acid is stronger acid than sulphuric acid. Explain.

Ans : The structures of perchloric acid ($HClO_4$) and sulphuric acid (H_2SO_4) are given below :



$HClO_4$ molecule



H_2SO_4 molecule

O.S. of Cl-atom in $HClO_4$ is +7 and that of S-atom in H_2SO_4 is +6. Since O.S. of Cl is higher than that of S, ClO_3 part of $HClO_4$ molecule pulls the electrons of O—H bond more strongly and hence O—H bond can break more easily to liberate H as proton (H^+) than SO_2 part in H_2SO_4. Thus $HClO_4$ is a stronger acid than H_2SO_4.

Q.7 Balance the following reaction taking place in alkaline medium.

$$\mathbf{Cl_2 + KIO_3 \longrightarrow Cl^- + KIO_4}$$

Ans : The skeleton oxidation and reduction half-reactions for the given reaction are :

$$\underset{(I\,=\,+5)}{KIO_3} \xrightarrow{\text{Oxidation}} \underset{(I\,=\,+7)}{KIO_4}$$

$$\underset{(Cl\,=\,0)}{Cl_2} \xrightarrow{\text{Reduction}} \underset{(Cl\,=\,-1)}{Cl^-}$$

Above half-reactions, in their balanced form, can be written as :

$$KIO_3 + 2OH^- \xrightarrow{\text{Oxidation}} KIO_4 + H_2O + 2e^-$$

$$Cl_2 + 2e^- \xrightarrow{\text{Reduction}} 2Cl^-$$

On adding : $KIO_3 + Cl_2 + 2OH^- \longrightarrow KIO_4 + 2Cl^- + H_2O$

Q.8 Write chemical equation for the reaction of alkaline perborate with Zn, giving tetrahydroxzincate anion.

Ans : In this reaction perborate ion, BrO_4^- (Br = +7) oxidises Zn(Zn = 0) to tetrahydroxo-zincate anion, $[Zn(OH)_4]^{2-}$ (Zn = +2) in alkaline medium and is itself gets reduced to bromate ion, BrO_3^- (Br = +5). Thus the two half-reactions can be written as :

$$Zn + 4OH^- \xrightarrow{\text{Oxidation}} [Zn(OH)_4]^{2-} + 2e^-$$

$$BrO_4^- + H_2O + 2e^- \xrightarrow{\text{Reduction}} BrO_3^- + 2OH^-$$

On adding : $Zn + 2OH^- + BrO_4^- + H_2O \longrightarrow [Zn(OH)_4]^{2-} + BrO_3^-$

Q.9 How is ammonium perchlorate (NH_4ClO_4) prepared ? What is the use of this compound ?

Ans : NH_4ClO_4 is obtained as a precipitate by treating in an aqueous solution of $NaClO_4$ with an aqueous solution of NH_4Cl.

$$NaClO_4 + NH_4Cl \longrightarrow NH_4ClO_4 + NaCl$$

NH_4ClO_4 is used as an oxidiser in solid rocket propellants in missiles.

Q.10 Complete the following equation

$$NaClO_3\ (aq) + SO_2\ (g) \xrightarrow{H_2SO_4} \text{.............}$$

Ans : $NaClO_3\ (aq) + SO_2\ (g) \xrightarrow{H_2SO_4} 2ClO_2\ (g) + Na_2SO_4\ (aq)$

Q.11 What happens when Cl_2 is passed through a solution of hot concentrated solution of a base like $Ba(OH)_2$?

Ans : $6Cl_2 + 6Ba(OH)_2\ (\text{conc}) \xrightarrow{\Delta} 5BaCl_2 + Ba(ClO_3)_2 + 6H_2O$

Q.12 Write the balanced equations for the following reactions :

(i) Sodium iodate is added to a solution of sodium bisulphite.

(ii) Iodate ion reacts with bisulphite ion to liberate I_2.

Ans : (*i*) The reaction between sodium iodate ($NaIO_3$) and sodium bisulphite ($NaHSO_3$) is a redox reaction in which $NaHSO_3$ (S = +4) is oxidised to $NaHSO_4$ (S = +6) and Na_2SO_4 (S = +6) while $NaIO_3$ (I = +5) gets reduced to I_2 (I = 0).

$$\underset{(I = +5)}{2NaIO_3} + \underset{(S = +4)}{5NaHSO_3} \longrightarrow \underset{(S = +6)}{3NaHSO_4} + \underset{(S = +6)}{2Na_2SO_4} + H_2O + \underset{(I = 0)}{I_2}$$

As a matter of fact the above reaction takes place through the following steps :

(*a*) $NaIO_3$ and $NaHSO_3$ combine together to produce HIO_3

$$NaIO_3 + NaHSO_3 \longrightarrow Na_2SO_3 + HIO_3\ ] \times 2 \qquad ...(i)$$

(*b*) HIO_3 produced as above gives nescent oxygen and is itself reduced to I_2.

$$2HIO_3 \longrightarrow I_2 + H_2O + 5O \qquad ...(ii)$$

On adding equations (*i*) and (*ii*), we get :

$$2NaIO_3 + 2NaHSO_3 \longrightarrow 2Na_2SO_3 + I_2 + H_2O + 5O \qquad ...(iii)$$

(*c*) Nescent oxygen as obtained in equation (*iii*) oxidises $NaHSO_3$ to $NaHSO_4$ and Na_2SO_3 to Na_2SO_4

$$\underset{(S\,=\,+4)}{NaHSO_3} + O \longrightarrow \underset{(S\,=\,+6)}{NaHSO_4}\ ] \times 3 \qquad ...(iv)$$

$$\underset{(S\,=\,+4)}{Na_2SO_3} + O \longrightarrow \underset{(O\,=\,+6)}{Na_2SO_4}\ ] \times 2 \qquad ...(v)$$

On adding equations (*iii*), (*iv*) and (*v*), we get :

$$2NaIO_3 + 5NaHSO_3 \longrightarrow I_2 + H_2O + 3NaHSO_4 + 2Na_2SO_4$$

(*Molecular equation*)

This molecular equation in its ionic form can be obtained as follows :

$$\underset{(I\,=\,+5)}{2IO_3^-} + 12H^+ + 10e^- \xrightarrow{\text{Reduction}} \underset{(I\,=\,0)}{I_2} + 6H_2O$$

$$\underset{(S\,=\,+4)}{HSO_3^-} + H_2O \xrightarrow{\text{Oxidation}} \underset{(S\,=\,+6)}{HSO_4^-} + 2H^+ + 2e^-\ ] \times 3$$

$$\underset{(S\,=\,+4)}{HSO_3^-} + H_2O \xrightarrow{\text{Oxidation}} \underset{(S\,=\,+6)}{SO_4^{2-}} + 3H^+ + 2e^-\ ] \times 2$$

On adding : $5HSO_3^- + 2IO_3^- \longrightarrow 3HSO_4^- + 2SO_4^{2-} + I_2 + H_2O$

(*ii*) The reaction between iodate ion (IO_3^-) and bisulphite ion (HSO_3^-) leading to the liberation of I_2 can be represented by the following ionic equation.

$$\underset{(I\,=\,+5)}{2IO_3^-} + \underset{(S\,=\,+4)}{HSO_3^-} \longrightarrow \underset{(S\,=\,+6)}{3HSO_4^-} + \underset{(S\,=\,+6)}{2SO_4^{2-}} + H_2O + \underset{(I\,=\,0)}{I_2}$$

University Questions

1. Write a note on "Oxides of iodine and fluorine". (*Madras 87*)
2. Describe the preparation and properties of the oxides of bromine. (*Bharathidasan 85*)
3. Write a short note on "Oxy-acids of chlorine". (*Raj. 86*)
4. Write a short note on bleaching powder. (*Jiwaji 85*)
5. What is available chlorine? Describe the chemistry involved in the method for the determination of percentage of available chlorine in a given sample of bleaching powder. (*Delhi 87; Agra 84*)