CHAPTER

31

Fertilisers

Fertilizers

What are Fertilizers ?

Fertilizers are the substances which are added to the soil in order to make up the deficiency of essential elements like nitrogen, phosphorus and potassium required for the growth of the plants.

Essential Qualities of a Good Fertilizer.

Every substance containing plant nutrients cannot be used as a fertilizer. However, the essential requisites of a good fertilizer are (*i*) The nutrient elements present in it must be readily available to the plants. (*ii*) It must be fairly soluble in water so as to enable it to dissolve in soil. (*iii*) By rain or water, the fertilizer must be converted into a form which the plant can assimilate easily. (*iv*) It must be stable so that it is available for a long time to the growing plant. (*v*) It should not be injurious to plants. (*vi*) It should be able to correct the acidity of the soil. (*vii*) It should be cheap.

Classification of Fertilizers.

Fertilizers are classified according to the nature of the element/elements like N, P or K they provide to the soil. This classification gives the following types of fertilizers

1. Nitrogenous fertilizers. These fertilizers mainly supply nitrogen to the plants or soil. $(NH_4)_2SO_4$, calcium ammonium nitrate (CAN), basic calcium nitrate, calcium cyanamide, urea etc. are the examples of nitrogenous fertilizers.

2. Phosphatic fertilizers. These fertilizers provide phosphorus to the soil. Superphosphate of lime, triple superphosphate and phosphate slag are the examples of phosphatic fertilizers.

3. Potash fertilizers. These fertilizers supply potassium to the plant. These are useful to the plants especially to mendow, glass, tobacco, cotton, coffee, potatoes and corn. All these fertilizers occur in nature. KCl, KNO_3, K_2SO_4 etc. are the important examples.

4. NP fertilizers. These fertilizers contain two elements namely nitrogen and phosphorus. These are obtained by mixing together nitrogenous and phosphatic fertilizers in suitable proportions. Examples of NP fertilizers are : *dihydrogen ammoniated phosphate*, $NH_4H_2PO_4$; *calcium superphosphate nitrate* $Ca(H_2PO_4)_2$, $2Ca(NO_3)_2$ and *ammoniated phosphate sulphate*, $(NH_4)H_2PO_4$, $(NH_4)_2SO_4$.

5. NPK or complete fertilizers. These fertilizers supply all the three essential elements namely nitrogen, phosphorus and potassium to the soil and are produced by mixing nitrogeneous, phosphatic and potash fertilizers in suitable proportions. It is observed that these fertilizers produce much better results. NPK fertilizers are mainly produced by *Zuari Agrochemicals Ltd; Goa.*

Important Fertilizers

1. Ammonium Sulphate or Sindri Fertilizer, $(NH_4)_2SO_4$.

This fertilizer is being manufactured at Sindri Fertilizer Factory, Sindri (Bihar) and hence is called *Sindri fertilizer.*

Manufacture (*i*) ***From air and steam : Sindri process.*** Air and steam are passed over red hot coke when a mixture of CO, N_2 and H_2 gases is formed.

$$C + \text{Air} \longrightarrow CO + N_2$$
$$C + H_2O \longrightarrow CO + H_2$$

The gaseous mixture of CO, N_2 and H_2 is then passed over hot Fe_3O_4 and Cr_2O_3 when CO gets oxidised to CO_2. The mixture of CO_2, N_2 and H_2 is then compressed to about 20 atmospheric pressure and passed into water in which CO_2 gets dissolved and is thus removed from the gaseous mixture. The remaining gases namely N_2 and H_2 are mixed together in the ratio of 1 : 3 and then converted into NH_3 by Haber's process. In Haber's process the mixture of H_2 and N_2 is heated to 450°–550°C, compressed to 150–200 atmospheric pressure and passed over hot Fe_2O_3, Al_2O_3 and K_2O mixture. Here Fe_2O_3 acts as a catalyst and the mixture of Al_2O_3 and K_2O acts as a promotor

$$N_2 + 3H_2 \underset{\substack{150\text{–}200 \text{ at. pressure} \\ (Fe_2O_3\, +\, Al_2O_3\, +\, K_2O)}}{\overset{\text{temperature} = 450\text{–}500°C}{\rightleftarrows}} 2NH_3 + \text{Heat}$$

Besides from Haber's process, NH_3 can also be obtained from coal distillation as is done at Sindri Fertilizer Factory. Now NH_3 gas is passed into a suspension of finely powdered $CaSO_4$ (calcined gypsum) in water through which a stream of CO_2 is also passed. CO_2 is obtained by heating $CaCO_3$.

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$2NH_3 + H_2O + CO_2 + CaSO_4 \longrightarrow \underset{\text{soluble}}{(NH_4)_2SO_4} + \underset{\text{ppt.}}{CaCO_3 \downarrow}$$

The precipitate of $CaCO_3$ is filtered off and the filtrate containing $(NH_4)_2SO_4$ is concentrated by evaporation under vacuum and cooled when crystals of $(NH_4)_2SO_4$ are obtained. These crystals are packed in jute bags and sold in the market under the name of *Sindri ferlilizer.*

$CaCO_3$ obtained as a by-product in this process is used as a raw material for the manufacture of cement and another fertilizer called *nitrochalk* which is a mixture of chalk and NH_4NO_3.

$CaSO_4$ used in the above reaction is obtained from Rajasthan where large deposits of gypsum occur.

The process described above is being carried out successfully at Sindri Fertilizer Factory, Sindri (Bihar). Hence the name *Sindri process.* Similar types of plants for the manufacture of $(NH_4)_2SO_4$ are also working in England, Germany, Austria, Italy and U.S.S.R.

***(ii)* From NH_3.** $(NH_4)_2SO_4$ is also made on a large scale by absorbing synthetic NH_3 gas in H_2SO_4.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$(NH_4)_2SO_4$ thus obtained is purified by crystallisation.

(iii) From ammonical liquir *In steel factories*, ammonium sulphate is obtained from ammoniacal liquor obtained as a by-product in the manufacture of coke by the dry distillation of coal. Then, it is heated with milk of lime whereby ammonia gas is passed into 20% sulphuric acid to get ammonium sulphate.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$
$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Besides organic compounds, ammoniacal liquor containts free NH_3 and ammonium salts which are of two types : *volatile* [*e.g.* $(NH_4)_2CO_3$, NH_4HS, NH_4CN etc.] and *fixed* [*e.g.* $(NH_4)_2SO_4$, NH_4Cl etc.]. Volatile salts are decomposed by boiling alone while fixed salts are decomposed by lime water, $Ca(OH)_2$. The total NH_3 in combination is about 17 g/litre. The ammoniacal liquor is heated in ammonia still (Fig. 31.1) first with steam to remove free and volatile NH_3 and then the residue is treated with lime water in order to decompose the fixed salts.

$$\begin{array}{ll} \textit{Volatile} & \left\{ \begin{array}{l} (NH_4)_2CO_3 \longrightarrow 2NH_3 + CO_2 + H_2O \\ (NH_4)_2HS \longrightarrow NH_3 + H_2S \end{array} \right. \\ \textit{salts} & \\ \textit{Fixed} & \left\{ \begin{array}{l} (NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow 2NH_3 + CaSO_4 + 2H_2O \\ 2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O \end{array} \right. \\ \textit{salts} & \end{array}$$

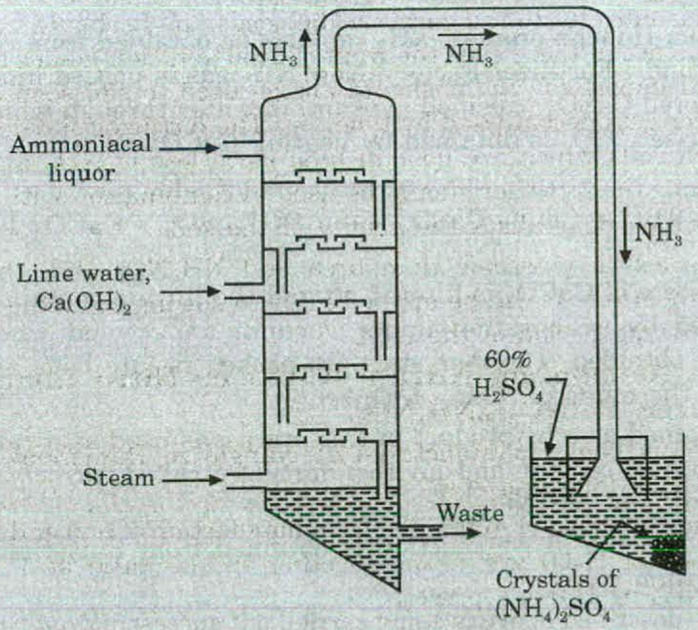


Fig. 31.1. Ammonia still used for the manufacture of $(NH_4)_2SO_4$

The mixture of NH_3 and steam so produced is passed through a lead-lined tank containing 60% H_2SO_4, when crystals of $(NH_4)_2SO_4$ separate on cooling.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

This method is being used in all the major steel plants in India, since ammoniacal liquor is obtained as a by-product in the manufacture of coke needed for the production of steel.

Manufacture in India. The fertilizer factories at Sindri, Durgapore, Bernpore, Jamshedpur, Bhilai, Alwaye, Bansjora, Digboi and Hanumangarh are manufacturing $(NH_4)_2SO_4$. Many other factories are being installed at various places for the production of $(NH_4)_2SO_4$.

Use of $(NH_4)_2SO_4$ as a Fertilizer. This fertilizer contains 24–25% NH_3 which is converted by nitrifying bacteria present in the basic soil into nitrates. These nitrates can be taken up by the plants easily from the soil.

$$(NH_4)_2SO_4 \xrightarrow[\text{in the soil}]{\text{Basic matters}} NH_3 \xrightarrow[\text{bacteria}]{\text{Nitrifying}} NO_3^-$$

This fertilizer is appropriate especially for rice and potato crops and basic soils. In acidic soils it should be used in combination with ground lime stone or chalk which neutralises the acidity the soil. Addition of NaCl has been found to increase the fertilising power of $(NH_4)_2SO_4$. This fertilizer may be applied prior to sowing or at the sowing time or during the growing period of the crop. After it is applied to the soil, it is absorbed and retained by soil particles and hence there is no danger of its being lost from the soil in drainage.

Methods of its application. The following precautions should be observed when $(NH_4)_2SO_4$ is being used as a fertilizer : (*i*) It should not be applied along with seeds as it is harmful to the germinating seeds. (*ii*) It should not be applied to wet clay soils, since in these soils the want of good aeration makes the nitrifying process slow and imperfect. (*iii*) It should not be used to soil soon after liming, since the fertilizer gets decomposed by lime. (*iv*) The fertilizer should not be used too frequently on soils which are poor in lime since loss of NH_3 makes the soil acidic. In such soils the fertilizer should be used in combination with ground lime stone or chalk which neutralises the acidity of the soil.

$(NH_4)_2SO_4$ is less hygroscopic than urea and NH_4NO_3 and, therefore, has better storage properties. It can be applied prior to sowing or at the sowing time or during the growing period of the crop.

2. Calcium Ammonium Nitrate (CAN) or Nitro Lime Stone or Nangal Fertilizer, $Ca(NO_3)_2.NH_4NO_3$.

This fertilizer is being manufactured at Nangal in Punjab by the process which consists of the following steps :

(*i*) Production of NH_3. N_2 (obtained from liquefaction of air) and H_2 (obtained by the electrolysis of H_2O) are mixed together in the ratio of 1 : 3 and are converted into NH_3 by Haber's process.

$$N_2 + 3H_2 \underset{\substack{150\text{–}200 \text{ at. pressure} \\ (Fe_2O_3 + Al_2O_3 + K_2O)}}{\overset{\text{temp.} = 450\text{–}500°C}{\rightleftarrows}} 2NH_3$$

***(ii)* Production of HNO_3.** A part of NH_3 produced as above is used in the manufacture of HNO_3 by the Ostwald's process. In this process NH_3 and air are mixed together in the ratio of 1 : 10 by volume. The mixture is introduced into a converter having a cage of fine platinum gauge (80 mesh) which is kept electrically heated between 820–920°C. By this treatment nitric oxide, NO is produced.

$$4NH_3 + 5O_2 \ (\textit{From air}) \underset{820\text{–}920°C}{\overset{\text{Pt guage}}{\rightleftarrows}} \underset{\substack{\text{Nitric} \\ \text{oxide}}}{4NO} + 6H_2O$$

NO is cooled and mixed with air so that NO is oxidised to nitrogen dioxide, NO_2. NO_2 is dissolved in H_2O to get the solution of HNO_3.

$$2NO + O_2 \ (\textit{From air}) \longrightarrow 2NO_3 \ (\textit{Nitrogen dioxide})$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

NO produced in the above reaction is reoxidised to NO_2 which can be used to prepare HNO_3 by dissolving it into H_2O as shown above.

***(iii)* Formation of NH_4NO_3.** Solution of HNO_3 obtained as above is concentrated and heated to about 75°C and is then allowed to fall in the form of a fine spray from the top of a tower called neutraliser while NH_3 gas pre-heated to about 70°C is introduced from the bottom of the neutraliser. This operation results in the neutralisation of HNO_3 by NH_3 and formation of NH_4NO_3.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

NH_4NO_3 is obtained in the form of a liquor at the bottom of the neutraliser. This liquor contains about 84% NH_4NO_3. This liquor is taken to vacuum concentrator where this liquor gets concentrated upto 92–94%.

***(iv)* Formation of calcium ammonium nitrate (CAN) pellets.** 92% concentrated solution of NH_4NO_3 is stirred with finely powdered lime stone ($CaCO_3$) in a granulator. The solution of NH_4NO_3 also contains some HNO_3 which reacts with lime stone to produce $Ca(NO_3)_2$ which, in turn, combines with NH_4NO_3 to form the pellets of calcium ammonium nitrate, $Ca(NO_3)_2.NH_4NO_3$.

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2$$

$$Ca(NO_3)_2 + NH_4NO_3 \longrightarrow \underbrace{Ca(NO_3)_2.NH_4NO_3}_{\substack{\text{Calcium ammonium} \\ \text{nitrate (CAN)}}}$$

Lime stone is added as a filler. Its function is to render NH_4NO_3 safe to handle, since NH_4NO_3 is an explosive substance.

***(v)* Coating of CAN pellets with soap stone.** Since CAN is very hygroscopic, it has to be protected from the atmospheric moisture during its transportation and storage. For this the pellets of CAN are stirred with concentrated solution of finely powdered soap stone (sodium silicate). This treatment produces a thin layer of soap stone on the surface of pellets. The pellets are dried and packed in polythene lined bags.

Manufacture in India. The fertilizer factories at Nangal (Punjab) and Rourkela are manufacturing calcium ammonium nitrate. The production of Nangal factory is 3.2 lac tons per year while the target production of Rourkela factory is 6 lac tons per year.

Use of CAN as a fertilizer. (*i*) CAN contains about 20% nitrogen.

(*ii*) It is directly assimilated by plants and does not undergo any changes in the soil.

(*iii*) It is highly soluble in water and as such finds its way into the soil very easily.

3. Basic Calcium Nitrate or Norwegian Salt Petre or Nitrate of Lime, $Ca(NO_3)_2.CaO$.

It is manufactured by a process which consists of the following two steps.

(*i*) Production of $CaNO_3$. When lime stone ($CaCO_3$) is neutralised by HNO_3 and the solution thus obtained is evaporated, monoclinic crystals of $Ca(NO_3)_2.4H_2O$ are obtained at ordinary temperature.

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + CO_2 + H_2O$$

(*ii*) Production of $Ca(NO_3)_2.CaO$. When $Ca(NO_3)_2$ is mixed with excess of quick lime (CaO), basic calcium nitrate, $Ca(NO_3)_2.CaO$ is obtained.

$$Ca(NO_3)_2 + CaO\ (\textit{Excess}) \longrightarrow \underbrace{Ca(NO_3)_2.CaO}_{\text{Basic calcium nitrate}}$$

Use of $Ca(NO_3)_2.CaO$ as a Fertiliser. Basic calcium nitrate is hygroscopic and is very soluble in water. It is basic in nature. It is directly assimilated by the plants and does not undergo any changes in the soil. It is less deliquescent than ordinary calcium nitrate, $Ca(NO_3)_2.4H_2O$ and hence is used in preference to $Ca(NO_3)_2.4H_2O$ as a fertiliser.

4. Calcium Cyanamide or Nitrolim, $CaCN_2$.

This compound is a derivative of cynamide, $H_2N—C = N$ or H_2CN_2 in which two hydrogen atoms have been replaced by one bivalent calcium atom.

Manufacture. Lime stone ($CaCO_3$) coal and air are the raw materials used in the manufacture of $CaCN_2$. The limestone is burnt in kilns to obtain lime (CaO). A mixture of lime and coal is heated in an electric furnace at 2500°C to produce CaC_2. CaC_2 so produced is finely powdered and then is heated in a cylindrical electric furnace at 1000°C in the atmosphere of N_2 under pressure obtained from air. By this operation $CaCN_2$ is formed.

$$\underset{\text{Lime stone}}{CaCO_3} \xrightarrow{\text{Heat}} \underset{\text{Lime}}{CaO} + CO_2$$

$$\underset{\text{Lime}}{CaO} + \underset{\text{Coal}}{3C} \xrightarrow[2500°C]{\text{Heat}} CaC_2 + CO$$

$$CaC_2 + N_2 \xrightarrow[1000°C]{Heat} \underbrace{CaCN_2 + C}_{\substack{\text{Nitrolim} \\ \text{(Grey)}}} + \text{Heat}$$

The grey mixture of $CaCN_2$ and C thus obtained is sold under the name of *nitrolim.*

Process. Since the reaction representing the formation of nitrolim is highly exothermic, the heating is done only at one time and the reaction further proceeds by itself. The heating is done in a cylindrical electric furnace (Fig. 31.2). The charge consisting of finely powdered CaC_2 is placed in the furnace and N_2 gas is passed from below. The electric current is passed through a thin carbon rod which is surrounded by a tube made of carbon board. On passing the electric current through the carbon rod, all the card board partitions get carbonised due to the production of heat, leaving openings through which N_2 can be freely circulated. The heat produced in the reaction is enough to maintain a temperature of 1000°C which is necessary for the reaction to proceed. After 36 hours, the reaction is complete.

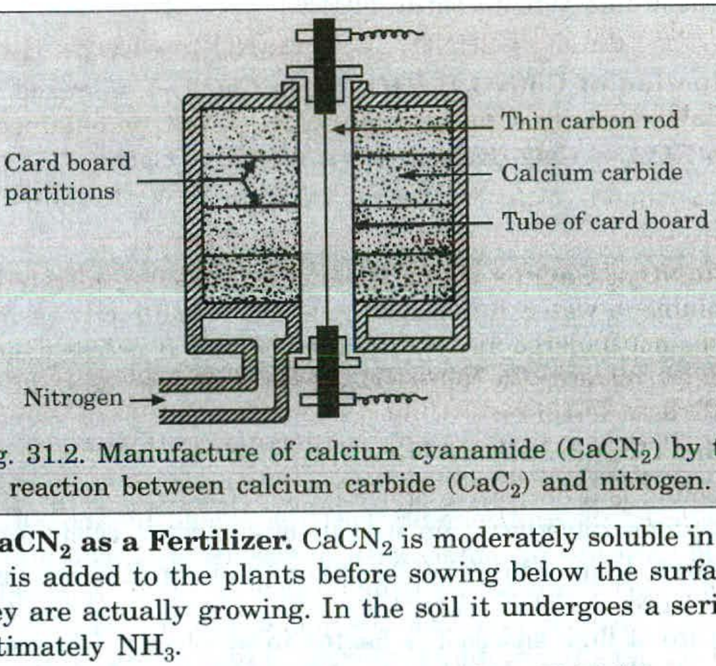


Fig. 31.2. Manufacture of calcium cyanamide ($CaCN_2$) by the reaction between calcium carbide (CaC_2) and nitrogen.

Use of $CaCN_2$ as a Fertilizer. $CaCN_2$ is moderately soluble in water and as a fertiliser it is added to the plants before sowing below the surface of soil and not when they are actually growing. In the soil it undergoes a series of changes producing ultimately NH_3.

$$CaN.CN + H_2O + CO_2 \longrightarrow CaCO_3 + \underset{\text{Cyanamide}}{H_2N.CN}$$

$$H_2N.CN + H_2O \longrightarrow \underset{\text{Urea}}{CO(NH_2)_2}$$

$$\underset{\text{Urea}}{CO(NH_2)_2} + H_2O \longrightarrow 2NH_3 + CO_2$$

NH_3 thus produced is converted into nitrates by the nitrifying bacteria and these nitrates are finally assimilated by plants. Since the conversion of $CaCN_2$ into NH_3 and that of NH_3 into nitrates by nitrifying bacteria takes place slowly,

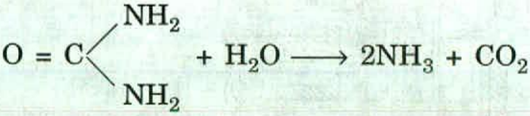
$CaCN_2$ is a slow acting fertilizer and is preferred to soluble compounds like $(NH_4)_2SO_4$ and $NaNO_3$ as it imparts fertility to the soil of a more permanent nature.

The formation of $CaCO_3$ during the reaction between $CaCN_2$ and moist CO_2 shown above is also useful from the agricultural point of view.

5. Urea or Carbamide, NH_2CONH_2.

Manufacture of urea can be studied from some standard book on Organic Chemistry.

Use of urea as a fertilizer. ***(a) Advantages of its Use.*** (*i*) Urea has the highest nitrogen content equal to 46.6%. This percentage of N_2 is much higher than that for $(NH_4)_2SO_4$ and CAN. Higher nitrogen content in urea results in economy in freight and packing. (*ii*) The cost of production of urea is relatively low since CO_2 required for its manufacture is obtained from crude naphtha. (*iii*) Urea is not subject to fire or explosion hazards as is NH_4NO_3 and hence there is no risk in the storage of urea. (*iv*) It does not change the pH of the soil. (*v*) Urea can be used to all types of crops and soils, since after its assimilation by plants through the interaction of nitrifying bacteria, it leaves behind only CO_2 in the soil. This CO_2 does no harm to the soil.



$$O=C(NH_2)_2 + H_2O \longrightarrow 2NH_3 + CO_2$$

On the other hand, $(NH_4)_2SO_4$ and CAN produce SO_4^{2-} and NO_3^- ions which make the soil acidic.

(b) Disadvantages of its use. (*i*) Urea is very soluble in H_2O and hygroscopic and hence requires better quality package than $(NH_4)_2SO_4$. (*ii*) It is not so stable as other solid nitrogenous fertilisers are, since urea decomposes even at lower temperatures, particularly in humid atmosphere, releasing NH_3 and CO_2. The formation of NH_3 and CO_2 results in serious loss. (*iii*) If urea contains impurities more than 2%, it cannot be used as a fertiliser since the impurities are toxic to certain crops, particularly to citrus crops.

(c) Methods of its application. (*i*) Urea should be applied at the sowing time. It should not come in contact with the seeds. (*ii*) It can also be applied as a top dressing. (*iii*) Since urea is highly concentrated, it should be used in combination with earth or sand before its application. (*iv*) It should not be applied when the soil contains free water or is likely to remain wet for three or four days after urea application.

6. Super-phosphate of Lime, or Calcium Super-phosphate, $[Ca(H_2PO_4)_2 + 2\ (CaSO_4.2H_2O)]$.

It is a mixture of *calcium dihydrogen phosphate* $Ca(H_2PO_4)_2$ and *dihydrate calcium sulphate (gypsum)*, $CaSO_4.2H_2O$.

Manufacture. It is manufactured by treating calcium phosphate (obtained from phosphate rock or bone ash) with calculated quantity of commercial (*i.e.*, chamber H_2SO_4.

$$\underset{\text{(Insoluble)}}{Ca_3(PO_4)_2} + 2H_2SO_4 + 4H_2O \longrightarrow \underbrace{\underset{\substack{\text{Calcium}\\ \text{dihydrogen}\\ \text{phosphate}}}{Ca(H_2PO_4)_2} + \underset{\text{Gypsum}}{2(CaSO_4.2H_2O)}}_{\text{Super-phosphate of lime}} + \text{Heat}$$

Plant and procedure. The plant used for the manufacture is shown in Fig. 31.3.

The phosphate rock is well powdered and is placed in a cast iron mixer. Now a calculated quantity of chamber H_2SO_4 is added to it. The whole mass is stirred by means of paddles for 2 to 5 minutes and then dumped mechanically into one of the brick-lined pits or dens D_1 or D_2 through the valves V_1 and V_2. Here the mixer is left for about 24 hours. The reaction which actually started in the mixer continues in the pot or den and the temperature gradually rises to 100–110°C because of the exothermic nature of the reaction. Since the phosphate rook invariably contains $CaCO_3$ and CaF_2 as impurities, they react with H_2SO_4 to evolve CO_2 and HF.

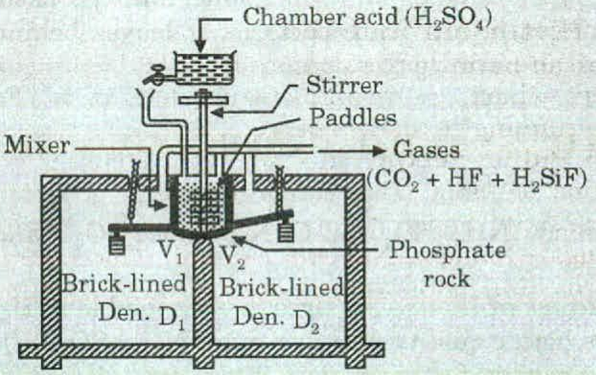


Fig. 31.3 Plant used for the manufacture of super-phosphate of lime, $Ca(H_2PO_4)_2 + 2(CaSO_4.2H_2O)$

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O$$
$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Free HF reacts with silica (SiO_2) present as impurity in the phosphate rock to produce SiF_4 which at once gets decomposed in presence of H_2O, forming hydrofluosilic acid, H_2SiF_6.

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$
$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + 2H_2SiF_6$$

The production of poisonous HF gas in the manufacture indicates that CaF_2 should not be present in large quantities in the phosphate rock. The presence of CaF_2 in large quantities also consumes huge quantities of extra H_2SO_4. The gases like CO_2, HF and H_2SiF_6 are led into a suitable absorption tower. As a result of the reaction, the mass becomes hard and is finally solidified to a porous dry solid due to the formation of gypsum. The mass is allowed to stand for a few days in the den until it becomes perfectly dry. The dried mass is removed from the den and is kept in the open for 4–6 weeks. During this period the excess of H_2SO_4 is completely consumed and the mass is completely dried. Finally the dry mass is crushed to a fine powder and is sold in the market under the name of *super-phosphate of lime.*

Use of super-phosphate of lime as a fertilizer. It contains about 16–20% of P_2O_5, depending on the purity of the phosphate rock used in the manufacture of the fertilizer and its active ingredient is calcium dihydrogen phosphate which is soluble in water. Thus it provides phosphate in a water-soluble form which is readily assimilated by the plants for their growth. In this respect it has an advantage over the normal calcium phosphate which is insoluble in water and cannot be assimilated by the plants.

Super-phosphate of lime has some disadvantages of its being used as a fertilizer. These disadvantages are : (*i*) It is relatively dilute fertiliser containing only 16–20% of P_2O_5 depending on the purity of the phosphate rock used in its manufacture. (*ii*) Being a dilute product, it requires relatively heavy freight and handling charges and a large number of expensive bags. (*iii*) It has a setting tendency and is converted into heavy lumps. (*iv*) The acidity in it causes the package to rot and contents to spill.

Manufacture of Fertilizers in India

In our country at present there are more than 60 factories in private as well as in public sectors which are manufacturing fertilizers. Following are the important factories running in the country.

1. Factories in Public Sector. The important factories of this type are: (*i*) Fertilizer Corporation of India. This corporation is a government undertaking and is running nine units under its management. These units are situated at Sindri (Bihar), Nangal (Punjab), Namrup (Assam), Gorakhpur (U.P.), Trombay (Maharashtra), Korba (M.P.), Barauni (Bihar), Talohar (Orissa) and Durgapur (West Bengal). (*ii*) The fertilizer and Chemical Travancore Ltd., Alwaye. (*iii*) Madras Fertilizer, Madras.

2. Factories in Private Sector. The important units being run by private sector are: (*i*) D.C.M. Chemical Works, Delhi and Kota. (*ii*) Indian Explosive Ltd., Kanpur. (*iii*) Zuari Agrochemicals Ltd., Goa. (*iv*) Coromandal Fertilizer Ltd., Visakhapatnam. (*v*) E.I.D. Parry's Ltd., Madras. (*vi*) Phosphate Company Ltd., Calcutta.

In 1982–83 the production of nitrogenous, phosphatic and potash fertilizer was 5.2 (in terms of nitrogen) 1.40 (in terms of P_2O_5) and 100 (in terms of K_2O) million tons. Although the number of factories manufacturing fertilizers is quite large, yet the production is too low to meet the total requirements of the country. In order to meet the increasing demand of fertilizers, 12 new factories being set up. Three of these have been set up at Bhatinda (Punjab), Panipat (Haryana) and Mathura (U.P.)

University Questions

1. Discuss the various methods for the fixation of nitrogen.
(*Indore 85; Jodhpur 85; Delhi 84*)

2. Give a brief account of the fertilizer industry in India.
(*Gorakhpur 81; Meerut 89*)

3. What are manures ? Name some natural and artificial manures.
(*Punjab 84*)

4. What is a fertilizer ? What is a mixed fertilizer ?
(Madras 85, 86; Jodhpur 84)

5. Give an account of different types of fertilizer.
(Madras 85, 86; Jodhpur 84)

6. Write a note on "Fertilizers and their maufacture in India".
(Bundelkhand 88)

7. Explain the following :
(*i*) Calcium superphosphate is a hotter fertilizer than triple superphosphate.
(Delhi 87; M.D. Rohtak 84)
(*ii*) A fertilizer that contains phosphorus has only limited utility.
(Bharathidasan 85)

8. Give the methods for the industrial preparation, properties and uses of :
(*i*) Calcium ammonium nitrate (CAN) *(Delhi 82, 89)*
(*ii*) Calcium cyanamide. *(Jiwaji 84)*
(*iii*) Urea. *(Delhi 88, 89)*
(*iv*) Calcium superphosphate. *(Delhi 87; M.D. Rohtak 84; Bundelkhand 88; Raj. 85; Meerut 89 S)*
(*v*) Triple superphosphate. *(Delhi 87; M.D. Rohtak 84)*
(*vi*) NPK fertilizers. *(Madras 85, 86; Jodhpur 84)*
(*vii*) $(NH_4)_2\ SO_4$. *(Delhi 82; Punjab 86; Poona 87)*

9. Write short note on CAN as a fertilizer. *(Himachal Pradesh 99, 2000)*

CHAPTER

32

Hydrides, Oxides and Oxyacids of Nitrogen

In this chapter we shall discuss the following compounds of nitrogen.

Hydrides

The well known hydrides of nitrogen are : (1) *Ammonia*, NH_3 (2) *Hydrazine*, $NH_2.NH_2$ or N_2H_4, and (3) *Hydrazoic acid*, HN_3. Out of these the first two hydrides are basic while the last one is acid'. Here we shall discuss only N_2H_4 and HN_3.

1. Hydrazine or Diammine, $NH_2.NH_2$ or N_2H_4.

This compound can be regarded as being formed by replacing one H-atom of NH_3 molecule by NH_2 group. This was first prepared by Curtius in 1889.

Preparation (*i*) *By Raschig's method* (1907). In this method a strong aqueous solution of NH_3 is boiled with sodium hypochlorite (NaOCl) in presence of a little glue or gelatin. The overall reaction can be represented as :

$$2NH_3 + \underset{\text{Sod. hypo-chlorite}}{NaOCl} \longrightarrow N_2H_4 + NaCl + H_2O$$

(*ii*) *Anhydrous* N_2H_4 is more easily prepared by adding a solution of sodium methoxide, CH_3ONa in methyl alcohol to a solution of hydrazine hydrochloride, $NH_2.NH_2.HCl$ in methyl alcohol, filtering off NaCl and distilling under reduced pressure when CH_3OH first distilles and then $NH_2.NH_2$.

$$NH_2.NH_2.HCl + CH_3ONa \longrightarrow NH_2.NH_2 + CH_3OH + NaCl$$

Properties. (*a*) **Physical.** Free hydrazine is colourless liquid, very hygroscopic and soluble in alcohol and water (bpt. 113.5°; m.pt. 1.4°). It is not very stable. On exposure to air, it readily absorbs carbon dioxide and moisture. It dissolves sulphur, arsenic, selenium and phosphorus.

(*b*) **Chemical.** (*i*) *Decomposition.* Hydrazine decomposes on heating into ammonia and nitrogen.

$$3NH_2.NH_2 \longrightarrow N_2 + 4NH_3$$

(*ii*) *Oxidation.* When heated in air, it gives nitrogen.

$$NH_2.NH_2 + O_2 \longrightarrow N_2 + 2H_2O$$

Ozone and hydrogen peroxide oxidise it to hydrazoic acid, N_3H,

$$3N_2H_4 + 5O_3 \longrightarrow 2N_3H + 5H_2O + 5O_2$$
$$3N_2H_4 + 5H_2O_2 \longrightarrow 2N_3H + 10H_2O.$$

(*iii*) *Reaction with sodium.* In the absence of oxygen, it reacts with sodium to form sodium hydrazine.

$$2NH_2NH_2 + 2Na \longrightarrow 2NH_2.NH.Na + H_2$$

(*iv*) It inflames in dry O_2 and reacts readily with halogens.

$$N_2H_4 + 2I_2 \longrightarrow 4HI + N_2$$

(*v*) *Basic nature.* It is a very weak base (much weaker than NH_3) and liberates, NH_3 from NH_4Cl. It forms two series of salts *viz. hydrazine monochloride*, $NH_2.NH_2.HCl$ and *hydrazine dichloride*, $ClH.NH_2.NH_2.HCl$

(*vi*) *Action of HNO_2.* It reacts with HNO_2, giving hydrazoic acid, HN_3

$$N_2H_4 + HNO_2 \longrightarrow HN_3 + 2H_2O.$$

(*vii*) *Formation of complexes.* Since N-atoms of N_2H_4 have a lone pair of electrons, N_2H_4 can act as a ligand and hence can form donor-acceptor complexes with metal ions like Ni^{2+}, Co^{2+} etc. The complexes given by this ligand with Ni^{2+} and Co^{2+} are $[Ni^{2+}(NH_2.NH_2)_4]^{2+}$ and $[Co^{2+}(NH_2.NH_2)]^{2+}$.

(*viii*) *Reducing properties.* Hydrazine and its salts are powerful reducing agents. For example :

(*a*) It precipitate Ag, Au and Pt from their salts.

$$4AgNO_3 + N_2H_4 \longrightarrow 4Ag + 4HNO_3 + N_2$$
$$4AuCl_3 + 3N_2H_4 \longrightarrow 4Au + 12HCl + 3N_2$$
$$PtCl_4 + N_2H_4 \longrightarrow Pt + 4HCl + N_2$$

(*b*) It reduces an alkaline solution of CuO (*i.e.* Fehling's solution) to Cu_2O.

$$4CuO + N_2H_4 \longrightarrow 2Cu_2O + 2H_2O + N_2$$

(*c*) It reduces I_2 to HI quantitatively in presence of $NaHCO_3$.

$$N_2H_4 + 2I_2 \rightleftarrows N_2 + 4HI$$

(*d*) It also reduces $KMnO_4$ in presence of dil. H_2SO_4.

$$4KMnO_4 + 6H_2SO_4 + 5N_2H_4 \longrightarrow 2K_2SO_4 + 4MnSO_4 + 16H_2O + 5N_2$$

The above reaction can be used for the titration of hydrazine and its salts.

(*e*) It reduces ferric salts to ferrous salts and iodates (IO_3^-) to iodides (I^-).

$$4Fe^{3+} + N_2H_4 \longrightarrow 4Fe^{2+} + 4H^+ + N_2$$
$$2IO_3^- + 3N_2H_4 \longrightarrow 2I^- + 6H_2O + 3N_2$$

(*f*) It reduces halogens to the corresponding halogen acids.

$$NH_2NH_2 + 2Cl_2 \longrightarrow N_2 + 4HCl$$
$$NH_2NH_2 + 2Br_2 \longrightarrow N_2 + 4HBr$$
$$NH_2NH_2 + 2I_2 \longrightarrow N_2 + 4HI$$

Thus hydrazine is on the one hand a base, and on the other hand it is a good reducing agent just in contrast to nitric acid which is a strong acid and powerful oxidising agent.

Uses. (*i*) An organic derivative of hydrazine known as *phenyl hydrazine*, $C_6H_5NH.NH_2$. has been largely used in the preparation of hydrazones, osazones and nitrogen ring compounds in organic chemistry. (*ii*) Hydrazine has recently been employed as a rocket fuel and as an anti-T.B. drug. (*iii*) It is also used as a reducing agent in analytical chemistry.

Structure. In structure hydrazine resembles H_2O_2 and is its *ammino analogue.*

HO—OH	H_2N—NH_2
Hydrogen peroxide	Hydrazine
(H_2O_2)	(N_2H_4)

If it is assumed that each nitrogen atom is sp^3 hybridised, it follows that there are two lone pairs of electrons in N_2H_4 molecule, one on each of the two nitrogen atoms. Raman spectra and high value of dipole moment (about 1.85 debye units) show that N_2H_4 has an *unsymmetrical structure* as shown in Fig. 32.1. In this structure NH_2 groups do not rotate freely. This is due to the tendency of the lone pairs of electrons to get as far apart as possible. In this molecule.

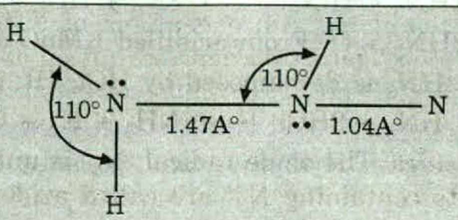


Fig. 32.1. Unsymmetrical structure of N_2H_4 molecule.

The N—N distance = 1.47 ± 0.02 Å, N—H distance = 1.04 Å and the NNH and HNH angles are about 110° each. The formation of two types of salts *viz.* : $NH_2NH_2.HCl$ and $ClH.NH_2NH_2.HCl$ can easily be explained on the basis of the above structure.

2. Hydrazoic Acid or Azoimide, NH_3.

Preparation. (*i*) *From sodamide.* When Na metal is heated to about 200°C and a current of dry NH_3 is passed over it, sodamide, $NaNH_2$ is obtained.

$$2Na + 2NH_3 \xrightarrow{200°C} 2NaNH_2 + H_2$$

When no more H_2 is evolved, in the same test tube is passed nitrous oxide (N_2O). This gives sodium azide, NaN_3 which on being distilled with dil. H_2SO_4 gives a solution of hydrazoic acid.

$$NH_2Na + N_2O \longrightarrow NaN_3 + H_2O$$
$$2NaN_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HN_3$$

The HN_3 solution obtained as above is fractionated and finally distilled over fused calcium chloride, when anhydrous acid is obtained.

(*ii*) *From hydrazine.* HN_3 can also be prepared by the careful oxidation of hydrazine ($NH_2.NH_2$) with NO, H_2O_2 or O_3.

$$3NH_2.NH_2 + 5O \longrightarrow 2HN_3 + 5H_2O$$

Properties. (*i*) HN_3 is a colourless volatile liquid with b.pt. = 37°. It is extremely poisonous and explosive and dissociates into N_2 and H_2 with the evolution of a large amount of heat.

$$2HN_3 \longrightarrow 3N_2 + H_2 + \text{Heat } (= 123.2 \text{ kcal})$$

(*ii*) *Reduction.* It is reduced to NH_3 or $NH_2.NH_2$ by sodium amalgam or finely divided platinum.

$$HN_3 + 4H_2 \longrightarrow 2NH_3$$
$$2HN_3 + 5H_2 \longrightarrow 2NH_2.NH_2$$

In acid solution, Ti (III), Cr (II) and Sn (II) readily reduce the acid.

$$Sn^{2+} + 3H^+ + HN_3 \longrightarrow Sn^{4+} + NH_4^+ + N_2$$

(*iii*) *Oxidation.* HNO_2, HOCl, Ce^{4+} ion and acidified $KMnO_4$ oxidise the acid to N_2 and these reactions can be used for the volumetric estimation.

$$HN_3 + HNO_2 \longrightarrow N_2 + N_2O + H_2O$$
$$2HN_3 + HOCl \longrightarrow 3N_2 + HCl + H_2O$$
$$2HN_3 + O \text{ (From acidified } KMnO_4) \longrightarrow 3N_2 + H_2O$$

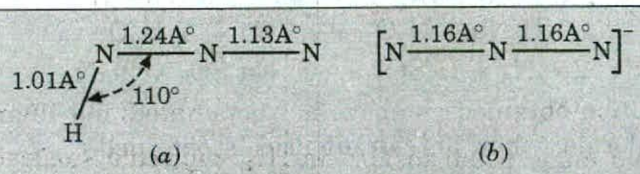
(*iv*) *Decomposition.* HN_3 is decomposed by HCl, HI, etc., giving N_2

$$HN_3 + 2HCl \longrightarrow NH_3 + N_2 + Cl_2$$

(*v*) *Formation of azides.* The azide radical, N_3^- is unknown in the free state or as a dimer. The salts containing N_3^- are called azides which are formed by various ways some of which are shown below :

$$3HN_3(aq) + M(M = Zn, Cu \text{ etc.}) \longrightarrow M(N_3)_2 + N_2 + NH_3$$
$$2HN_3(aq) + Mg \longrightarrow Mg(N_3)_2 + H_2$$
$$2HN_3 \text{ (in ether)} + AlH_3 \longrightarrow Al(N_3)_3 + 3H_2$$
$$HN_3 \text{ (vapour)} + AgNO_3\text{(solution)} \longrightarrow AgN_3 \downarrow + HNO_3$$
$$HN_3 + NH_3 \longrightarrow [NH_4]^+N_3^- \text{ (Ammonium azide)}$$
$$HN_3 + N_2H_4 \longrightarrow [N_2H_5]^+N_3^- \text{ (Hydrazonium azide)}$$

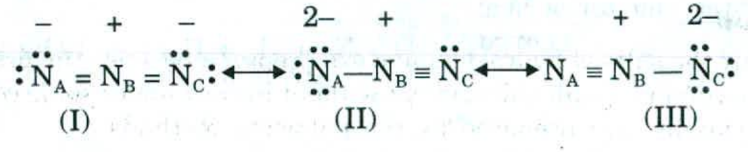
Structure of HN_3 molecule and N_3^- ion. HN_3 molecule has an unsymmetrical (bent) structure with linear N—N—N skeleton while the X-ray and electron diffraction studies of the ionic metal azides have shown that N_3^- ion in these azides has symmetrical structure with linear N—N—N skeleton, *i.e.* all the N-atoms in N_3^- ion lie in a straight line with both bond lengths equal to 1.16 A° (See Fig. 32.2).



(*a*) (*b*)

Fig. 32.2. (*a*) Unsymmetrical (bent) structure of HN_3 molecule (*b*) Symmetrical structure of azide ion, N_3^-.

Electron structure of N_3^- ion is a resonance hybrid of the following three structures :



$$\overset{-}{:\ddot{N}_A} = \overset{+}{N_B} = \overset{-}{\ddot{N}_C:} \longleftrightarrow \overset{2-}{:\underset{\cdot\cdot}{\ddot{N}_A}} — \overset{+}{N_B} \equiv \ddot{N}_C \longleftrightarrow N_A \equiv \overset{+}{N_B} — \overset{2-}{\underset{\cdot\cdot}{\ddot{N}_C}:}$$

(I) (II) (III)

All the three N-atoms in structure (I) use *sp* hybrid orbitals to form σ-bonds. Each of the terminal N-atoms (N_A and N_C atoms) has a lone pair of electrons in one of the *sp* hybrid orbitals. The formation of two σ- and two π-bonds in N_3^- ion has been shown in Fig. 32.3. σ-bonds are *sp—sp* σ-bonds while π-bonds are ($p\pi$—$p\pi$) π-bonds.

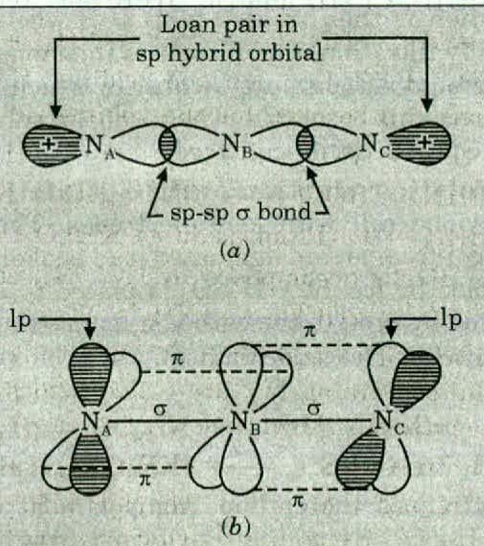


Fig. 32.3. Formation of (*a*) two σ-bonds (*b*) to π-bonds in Ni_3^- ion, σ-bonds are *sp—sp* σ-bonds while π-bonds are *p–p* π-bonds.

For the acid, HN_3 itself which is largely covalent the following three resonance structures *viz.* (A), (B) and (C) corresponding to the above three structures *viz.* (I), (II) and (III) may be written, but one of these structures *viz.* structure (C) is excluded, since in this structures two adjacent N-atoms have the same charge which is against the Pauling's adjacent charge rule. Thus HN_3 is a resonance hybrid of structures (A) and (B) only and structure (C) is a wrong structure.

$$\underset{\mathrm{H}}{\ddot{N}_A}=\overset{+}{N_B}=\overset{-}{\ddot{N}_C}: \leftrightarrow :\underset{\mathrm{H}}{\overset{-}{\ddot{N}_A}}-\overset{+}{N_B}\equiv\ddot{N}_C\,; \quad \underset{\mathrm{H}}{\overset{+}{N}}\equiv\overset{+}{N}-\overset{2-}{\ddot{\underset{\cdot\cdot}{N}}}:$$

(A) (B) (C)(Wrong structure)

H–N_A–N_B bond angle equal to 110° in HN_3 molecule suggests that both the end N-atoms in structure (A) are sp^2 hybridised. One of the three sp^2 hybrids on N-atom linked with H-atom has a lone pair of electrons.

Hydroxylamine, NH_2OH

It is a hydroxy derivative of NH_3 and was discovered by Lossen in 1865.

Preparation.

As a rule only the salts of hydroxylamine are prepared because the preparation of the free hydroxylamine is difficult and not without hazard under some conditions. Salts of hydroxylamine are prepared by the following methods :

***(i)* By the reduction of NO with nascent hydrogen.** Nitric oxide (NO) is passed through mixture of granulated tin and conc. HCl when hydroxylamine hydrochloride, $NH_2OH.HCl$ or $[NH_3OH]Cl$ and a little of NH_4Cl are formed.

$$NO + 3H \longrightarrow NH_2OH$$
$$NH_2OH + HCl \longrightarrow NH_2OH.HCl$$

The resulting solution is then treated with H_2S when tin is precipitated as SnS which is removed by filtration. The filtrate is then evaporated to dryness and the dry mass is extracted with absolute alcohol in which only $NH_2OH.HCl$ gets dissolved and NH_4Cl remains insoluble. The alcoholic solution is finally treated with ether when $NH_2OH.HCl$ is precipitated.

***(ii)* By the electrolytic reduction of HNO_3 (Tafel, 1902).** The electrolysis is carried out in a divided cell with lead electrodes. The cooled lead anode is separated by a porous pot from an amalgamated lead beaker which acts as cathode. The whole thing is cooled by ice. 50% H_2SO_4 is placed in each compartment and 50% HNO_3 is added drop by drop to the cathodic compartment Cathodic reduction of HNO_3 gives HN_2OH which reacts with H_2SO_4 to give hydroxylamine sulphate, $(NH_2OH)_2.H_2SO_4$.

$$HNO_3 + 6H \longrightarrow NH_2OH + 2H_2O$$
$$2NH_2OH + H_2SO_4 \longrightarrow (NH_2OH)_2.H_2SO_4$$

At the end of electrolysis the cathode compartment contains a solution of $(NH_2OH)_2.H_2SO_4$ and H_2SO_4. By adding $BaCl_2$ and filtering off the precipitated $BaSO_4$, a solution of $NH_2OH.HCl$ is obtained.

$$(NH_2OH)_2.H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{solution}}{2(NH_2OH.HCl)} + \underset{\text{ppt.}}{BaSO_4}$$

Preparation of Anhydrous Hydroxylamine.

(i) It was prepared by Lobry de.Bruyn in 1891 by treating a solution of hydroxylamine hydrochloride in methyl alcohol with a solution of sodium methoxide in methyl alcohol.

$$CH_3ONa + NH_2OH.HCl \longrightarrow CH_3OH + NaCl + NH_2OH$$

The sodium chloride was filtered off and the methyl alcohol separated by distillation under reduced pressure.

(ii) The anhydrous hydroxylamine is also formed by heating hydroxylamine orthophosphate to 125° under low pressure.

$$(NH_2OH)_3.H_3PO_4 \longrightarrow 3NH_2OH + H_3PO_4$$

Physical Properties.

It is hard needle-like white substance, melting at 33° and boiling at 58° at 22 mm pressure. It decomposes at the steam temperature. It is readily soluble in water but not much in alcohol. It can be crystallised out from its ethereal solution. Its solution in water is a weak base.

$$NH_2OH + H_2O \longrightarrow \underset{\text{Hydroxylamonium ion}}{NH_3OH^+} + OH^-$$

Chemical Properties.

(i) **Explosive nature** *(a)* It explodes with halogens.

$$2NH_2OH + 2Cl_2 \longrightarrow N_2O + H_2O + 4HCl$$

(*b*) It also explodes with permanganate and dichromate.

(*ii*) **Stability.** It is very unstable and the solid decomposes slowly above 15°C.

$$3NH_2OH \longrightarrow N_2 + NH_3 + 3H_2O$$
$$4NH_2OH \longrightarrow N_2O + 2NH_3 + 3H_2O$$

(*iii*) **Action of HNO_3 and HNO_2.** NH_2OH when heated with HNO_3 gives nitric oxide, NO

$$NH_2OH + HNO_3 \longrightarrow 2NO + 2H_2O$$

But with HNO_2 it gives nitrous oxide, N_2O

$$NH_2OH + HNO_2 \longrightarrow \underset{\text{Hyponitrous acid}}{H_2N_2O_2} + H_2O$$

$$H_2N_2O_2 \longrightarrow N_2O + H_2O$$

(*iv*) **Basic nature.** It is soluble in water and the resulting solution is a weak monoacid base (even weaker than NH_3).

$$NH_2OH + H_2O \rightleftarrows \underset{\text{Hydroxyl-amonium cation}}{[NH_3OH]^+} + OH^-$$

$[NH_3\ OH]^+$ cation is comparable to NH_4^+ ion. NH_2OH forms salts with acids which are formulated as the addition compounds of NH_2OH and the acid. For example hydroxylamine hydrochloride and hydroxylamine sulphate are formulated as $NH_2OH.HCl$ and $(NH_2OH)_2.H_2SO_4$ respectively.

(*v*) **Reducing properties.** In acidic medium, NH_2OH is powerful reducing agent. Potential equation is :

$$2NH_2OH \longrightarrow N_2O + H_2O + 4H$$

Thus it reduces :

(*a*) Fehling's solution (CuO) to a red precipitate of Cu_2O.

$$2CuO + 2H \longrightarrow Cu_2O + H_2O$$

(*b*) $AuCl_3$ to metallic Au

$$AuCl_3 + 2H \longrightarrow Au + 3HCl$$

(*c*) Fe (III) salts to Fe (II) salts

$$Fe^{3+} + H \longrightarrow Fe^{2+} + H^+$$

(*e.g.*, $FeCl_3 + H \longrightarrow FeCl_2 + HCl$)

(*d*) Halogens (X_2) to the corresponding halogen acids (HX)

$$X_2 + 2H \longrightarrow 2HX$$

Generally explosion occurs in the above reduction reactions.

(*vi*) **Oxidising properties.** In *alkaline medium*, NH_3OH acts as an oxidising agent. The potential equation is :

$$NH_2OH \longrightarrow NH_3 + O$$

Thus it oxidises :

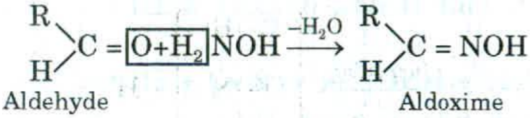
(*a*) $Fe(OH)_2$ to $Fe(OH)_3$

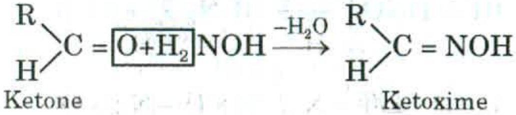
$$2Fe(OH)_2 + H_2O + O \longrightarrow 2Fe(OH)_3$$

(*b*) Sodium arsenite, Na_3AsO_3 to sodium arsenate, Na_3AsO_4

$$Na_3\ AsO_3 + O \longrightarrow Na_3AsO_4$$

(*vii*) **Reaction with aldehydes and ketones.** NH_2OH reacts with aldehydes and ketones to give oximes.



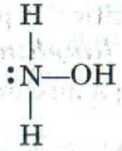


Uses.

It is used as a reagent in organic chemistry.

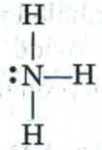
Structure.

It has been given the following structure (I) which is similar to that of NH_3 (II)



$$:\overset{\displaystyle H}{\underset{\displaystyle H}{N}}-OH$$

(I)

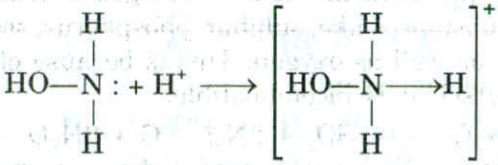


$$:\overset{\displaystyle H}{\underset{\displaystyle H}{N}}-H$$

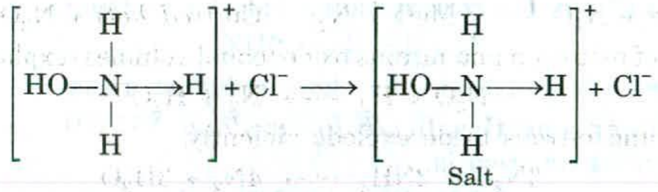
(II)

It is quite obvious that N-atom has a lone pair. In the reaction with an acid (say HCl) the lone pair gets attached with the H^+ ion obtained from the acid. Thus :

$$HCl \longrightarrow H^+ + Cl^-$$



$$HO-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}: + H^+ \longrightarrow \left[HO-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}\longrightarrow H\right]^+$$

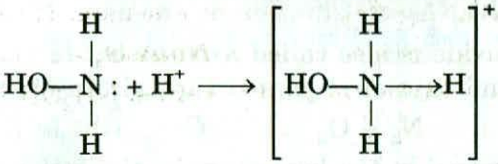


$$\left[HO-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}\longrightarrow H\right]^+ + Cl^- \longrightarrow \left[HO-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}\longrightarrow H\right]^+ + Cl^-$$

Salt

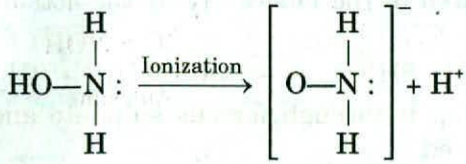
Structure (I) which is that of NH_2OH can also explain the behaviour of the molecule to act as a base, as an acid and as an oxidising agent as shown below :

(a) *As a base* :



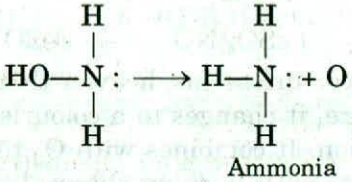
$$HO{-}\overset{H}{\underset{H}{N}}: + H^+ \longrightarrow \left[HO{-}\overset{H}{\underset{H}{N}}{\rightarrow}H\right]^+$$

(b) *As an acid* :



$$HO{-}\overset{H}{\underset{H}{N}}: \xrightarrow{\text{Ionization}} \left[O{-}\overset{H}{\underset{H}{N}}:\right]^- + H^+$$

(c) *As an oxidising agent* :



$$HO{-}\overset{H}{\underset{H}{N}}: \longrightarrow \underset{\text{Ammonia}}{H{-}\overset{H}{\underset{H}{N}}:} + O$$

Oxides

1. Nitrous Oxide, N_2O.

When this oxide is inhaled in small quantities, it produces hysterical laughter and for this reason this oxide is also called ***laughing gas***.

Preparation. N_2O is prepared by heating a mixture of $NaNO_3$ and $(NH_4)_2SO_4$.

$$2NaNO_3 + (NH_4)_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2N_2O + 4H_2O$$

Properties. Nitrous oxide is a colourless gas, having a faint sweetish smell and a sweet taste. When inhaled for long, it produces insensibility. Large quantities may prove fatal. It is soluble in water (63 volumes at 20°C) and the solution has a sweetish taste. That is why it is collected over hot water. It is heavier than air (vapour density 22). It can be easily liquefied at 0°C and a pressure of 30 atmospheres. The liquid boils at –89.5°C. The gas is neutral to litmus. It supports the combustion of substances like, sulphur, phosphorus, sodium, magnesium, candle and a splinter just as well as oxygen. This is because of its ready decomposition into its elements. Itself it is incombustible.

$$S + 2N_2O \longrightarrow SO_2 + 2N_2; \quad C + 2N_2O \longrightarrow CO_2 + 2N_2$$

$$2P + 5N_2O \longrightarrow P_2O_5 + 5N_2; \quad 2Na + N_2O \longrightarrow Na_2O + N_2$$

$$Mg + N_2O \longrightarrow MgO + N_2; \quad Cu\ (\textit{red hot}) + N_2O \longrightarrow CuO + N_2$$

A mixture of hydrogen and nitrous oxide (equal volumes) explodes with violence.

$$N_2O + H_2 \longrightarrow N_2 + H_2O$$

Ammonia and nitrous oxide explode violently.

$$3N_2O + 2NH_3 \longrightarrow 4N_2 + 3H_2O$$

Uses. Nitrous oxide is used (*i*) as the propellant gas in *whipped cream bombs.* (*ii*) as a mild anaesthetic in dental and other minor surgical operations when mixed with 10% oxygen.

2. Nitric Oxide, NO.

Preparation. This oxide is also called ***nitrous oxide*** and is produced when a mixture of nitrogen and oxygen is passed through an electric arc.

$$N_2 + O_2 \rightleftarrows 2NO$$

The gas may be prepared in the laboratory by the action of cold dilute nitric acid on copper.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

It is purified by passing it through ferrous sulphate and heating the black compound $FeSO_4.NO$ formed.

$$FeSO_4.NO \xrightarrow{\Delta} FeSO_4 + NO$$

Properties. It is a colourless gas, heavier than air and very sparingly soluble in water. Under pressure, it changes to a colourless liquid at –151°C. The gas is neutral to litmus solution. It combines with O_2 to form brown fumes of nitrogen peroxide (NO_2). It reacts with burning charcoal, S, P to give oxides.

$$2NO + O_2 \longrightarrow 2NO_2;\ 2NO + C \longrightarrow N_2 + CO_2$$
$$2NO + S \longrightarrow N_2 + SO_2;\ 10NO + 4P \longrightarrow 2P_2O_5 + 5N_2$$

NO reacts with ferrous sulphate, potassium sulphate etc. to form addition products.

$$FeSO_4 + NO \longrightarrow \underset{\text{Nitroso ferrous sulphate}}{[Fe(NO)]SO_4} \text{ or } FeSO_4.NO$$

$$K_2SO_4 + 2NO \longrightarrow \underset{\text{Nutroso potaesium sulphate}}{K_2SO_4.2NO}$$

$$HCl + NO \longrightarrow \underset{\text{Nitrosonium chloride}}{NO.HCl} \text{ or } [NOH]Cl$$

It reduces acidified solution of $KMnO_4$ to $MnSO_4$ and HNO_3 to NO_2.

$$6KMnO_4 + 9H_2SO_4 + 10NO \longrightarrow 3K_2SO_4 + 6MnSO_4 + 10HNO_3 + 4H_2O$$
$$2HNO_3 + NO \longrightarrow 3NO_2 + H_2O$$

It oxidises SO_2 to H_2SO_4 and H_2S to S.

$$2NO + SO_2 + H_2O \longrightarrow H_2SO_4 + N_2O;$$
$$H_2S + 2NO \longrightarrow H_2O + S + N_2O$$

It combines with Cl_2 and Br_2 to form nitrosyl chloride (NOCl) and nitrosyl bromide (NOBr) respectively.

Uses. The gas is used (*i*) for the manufacture of nitric acid. (*ii*) as a catalyst in the lead chamber process for the manufacture of sulphuric acid. (*iii*) to distinguish oxygen from, nitrous oxide.

3. Dinitrogen Trioxide, N_2O_3.

This oxide is also called ***nitrogen sesquioxide.*** It is also called ***nitrous anhydride***, *i.e.* anhydride of HNO_2, since it gives HNO_2 when treated with H_2O.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

Preparation. Nitrogen trioxide is prepared by the reduction of nitric acid with arsenious oxide

$$As_2O_3 + 2HNO_3 + 2H_2O \longrightarrow N_2O_3 + 2H_3AsO_4$$

Properties. It is a red coloured gas. On condensing, it gives a dark blue liquid. It is acidic in nature and reacts with sodium hydroxide to form sodium nitrite.

$$2NaOH + N_2O_3 \longrightarrow 2NaNO_2 + H_2O$$

On heating it is dissociated to nitric oxide (NO) and nitrogen peroxide (NO_2).

$$N_2O_3 \xrightarrow{\Delta} NO + NO_2$$

4. Nitrogen Dioxide $\rightleftharpoons$ Dinitrogen Tetroxide, $2NO_2 \rightleftharpoons N_2O_4$.

This oxide is also called ***nitrogen peroxide***. Since it gives a mixture of HNO_3 and HNO_2, it is also called ***mixed acid anhydride*** *i.e. anhydride of* HNO_2 *and* HNO_3.

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

Preparation. NO_2 is prepared by the action of heat on $Pb(NO_3)_2$ (laboratory preparation) or by the action of Cu on conc. HNO_3.

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$$

$$Cu + 4HNO_3 \longrightarrow Cu\ (NO_3)_2 + 2NO_2 + 2H_2O$$

Properties. Nitrogen dioxide is a reddish-brown gas with a pungent smell. At 14°C it has a *deep brown* colour and a density which corresponds to the formula, NO_2. As the temperature falls, its colour goes on fading. On further cooling, it condeneses to a *pale-yellow* liquid (b.p. = 22°C) which freezes to *colourless* crystals (m.p. = −9°C). The density of the solid corresponds to the formula. N_2O_4. Quite evidently, *progressive association of the molecules occurs with the decrease in temperature.*

$$2NO_2 \rightleftarrows N_2O_4$$

The colour of nitrogen dioxide begins to fade above 140°C also. This is due to its dissociation into nitric oxide (NO) and oxygen (O_2).

$$2NO_2 \rightleftharpoons 2NO + O_2$$

The dissociation is complete at 620°C when the gas becomes completely colourless. These changes are reversed on cooling.

$$\underset{\substack{\text{Solid}\\\text{(Colourless)}}}{N_2O_4} \overset{-90^\circ}{\rightleftharpoons} \underset{\substack{\text{Liquid}\\\text{(Pale-yellow)}}}{N_2O_4} \overset{22^\circ}{\rightleftharpoons} \underset{\substack{\text{Vapour}\\\text{(Pale-yellow)}}}{N_2O_4} \overset{140^\circ}{\rightleftharpoons} \underset{\substack{\text{Gas}\\\text{(Reddish-}\\\text{brown)}}}{2NO_2} \overset{620^\circ}{\rightleftharpoons} \underbrace{2NO + O_2}_{\substack{\text{Gaseous}\\\text{mixture}\\\text{(Colourless)}}}$$

At any temperature below 22° and 140°, the gas exists as an equilibrium mixture of *coloured* NO_2 molecules and *colourless*, N_2O_4 molecules.

$$2NO_2 \rightleftharpoons N_2O_4$$

It is soluble in water. This can be shown by *fountain experiment.* It is much denser than air and can be *poured* downwards like CO_2. It is poisonous and sets up septic pneumonia, if inhaled. It also corrodes the skin.

It is acidic towards litmus. When dissolved in water, it forms a mixture of nitrous and nitric acids. It is, therefore, a *mixed anhydride*.

$$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$$

It neutralizes alkali solution with the formation of mixture of alkali nitrate and nitrite, thus proving its acidic nature.

$$2NaOH + 2NO_2 \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

It supports the combustion of brightly being phosphorus, but does not support the combustion of candle, a splinter or sulphur. Metals like iron and tin burn in it when heated to 500°C.

It acts as a strong *oxidising agent*. Thus :

(*a*) It liberates iodine from potassium iodide, and turns starch iodide paper blue.

$$2KI + 2NO_2 \longrightarrow 2KNO_2 + I_2.$$

(*b*) Suphuretted hydrogen is oxidised to sulphur and carbon monoxide to carbon dioxide.

$$NO_2 + H_2S \longrightarrow NO + H_2O + S$$
$$CO + NO_2 \longrightarrow CO_2 + NO$$

(*c*) Ferrous sulphate is oxidised to ferric sulphate.

$$2FeSO_4 + H_2SO_4 + NO_2 \longrightarrow Fe_2(SO_4)_3 + H_2O + NO$$

Due to the combination of the nitric oxide formed with the unreacted ferrous sulphate, the whole mass turns black.

(*d*) It oxidises metals like potassium, sodium, mercury and tin. Finely divided copper gives cuprous oxide which then absorbs more of it forming *"nitro copper"*.

$$NO_2 + 2Na \longrightarrow Na_2O + NO$$
$$NO_2 + 2K \longrightarrow K_2O + NO$$
$$2Cu + NO_2 \longrightarrow Cu_2O + NO$$

(*e*) Phosphorus, sulphur and charcoal burn in it to form their oxides.

$$5NO_2 + 2P \xrightarrow{\text{heat}} P_2O_5 + 5NO$$

$$2NO_2 + S \xrightarrow{\text{heat}} SO_2 + 2NO$$

$$2NO_2 + C \xrightarrow{\text{heat}} 2O_2 + 2NO$$

(*f*) A mixture of carbon disulphide and nitrogen dioxide explodes violently.

$$2CS_2 + 6NO_2 \longrightarrow 2CO_2 + 4SO_2 + 3N_2$$

(*g*) Hydrogen reacts with NO_2 in the presence of catalysts like platinum or finely divided nickel to give ammonia and water.

$$7H_2 + 2NO_2 \xrightarrow{\text{heat}} 2NH_3 + 4H_2O$$

It reduces ozone to oxygen and is itself oxidized to nitrogen pentoxide.

$$N_2O_4 + O_3 \longrightarrow N_2O_5 + O_2$$

Uses. It is used (*i*) as a catalyst in the manufacture of H_2SO_4 by lead chamber process. (*ii*) in the production of HNO_2. (*iii*) as a rocket fuel.

5. Nitrogen Pentoxide, N_2O_5.

This oxide is also called ***nitric anhydride***, *i.e.* anhydride of HNO_3, since it makes HNO_3 with H_2O

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

Preparation. Nitrogen pentoxide is prepared by distiling concentrated nitric acid over phosphorus pentoxide

$$2HNO_3 + P_2O_5 \longrightarrow 2HPO_3.$$

The vapours of N_2O_5 so obtained are cooled in a U-tube which is cooled by solid carbon. dioxide and ether.

It is also obtained by passing dry chlorine over solid silver nitrate at 95°C and as soon as the reaction starts, cooling the mixture to 60°C.

$$4AgNO_3 + 2Cl_2 \longrightarrow 4AgCl + 2N_2O_5 + O_2$$

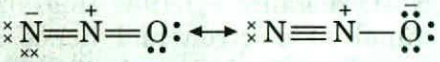
Properties. N_2O_5 forms colourless hard crystals which are deliquescent and which melt at 30°C. N_2O_5 is very unstable and may explode even without heating. It decomposes to give nitrogen dioxide and oxygen. It dissolves in water with a hissing giving nitric acid and is, therefore, called *nitric anhydride.*

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$
$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

Structure of Oxides

1. Nitrous Oxide, N_2O.

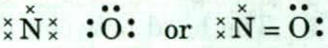
Nitrous oxide is a linear and unsymmetrical molecule with a very small value of dipole moment (= 0.116D). Thus N_2O molecule is a resonance hybrid of the two structures shown in the margin.



$${}^{\times}_{\times}\underset{\times\times}{\overset{-}{N}}=\overset{+}{N}=\underset{\bullet\bullet}{O}{:} \longleftrightarrow {}^{\times}_{\times}N\equiv\overset{+}{N}-\overset{-}{\ddot{\underset{\bullet\bullet}{O}}}{:}$$

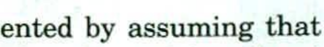
2. Nitric oxide, NO.

According to valence bond theory, NO molecule is an *odd electron* molecule, since it contains an odd number of electrons (= 11 electrons = 5 from N-atom + 6 from O-atom). NO molecule in the *gaseous state* has one unpaired electron which makes this molecule paramagnetic. Thus its structure can be represented as shown in the margin. Since the observed nitrogen–oxygen bond length (= 1.14 A°) is in between that of a N = O bond (= 1.15 A°) and N ≡ O (= 1.05 A°), the true structure of NO molecule is supposed to be a resonance hybrid of the structures shown in the margin. According to magnetic evidence the odd electron in NO molecule spends half of its time on N-atom and half of its time on O-atom. This situation can be represented by assuming that NO molecule contains one *three-electron bond* [represented as (3c—2e) bond] and two *two-electron bonds* [represented as (2c—2e) bond] as shown in the margin.



$${}^{\times}_{\times}\overset{\times}{N}{}^{\times}_{\times}\ \ {:}\ddot{O}{:}\ \text{or}\ {}^{\times}_{\times}\overset{\times}{N}=\ddot{O}{:}$$

Structure of nitric oxide molecule, NO



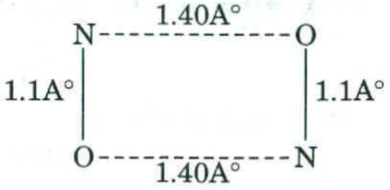
$${}^{\times}_{\times}\overset{\times}{N}=\ddot{O}{:} \longleftrightarrow {}^{\times}_{\times}\overset{-}{\overset{\times\times}{N}}=\overset{+}{\dot{O}}{:}$$

(3c—2e) bond is about half as strong as a normal (2c—2e) bond. This structure is in agreement with small value of dipole moment (= 0.16 D) of NO molecule.

X-ray analysis has shown that in the *solid state* NO molecule contains *rectangular dimers* whose dimensions are given in the margin.

The structure of NO molecule has also been explained on the basis of molecular orbital theory as discussed on page 602 in Chapter 8.

NO molecule contains one (3c–2c) and two (2c–2e) bonds.



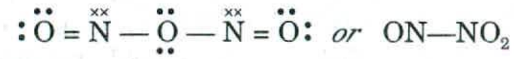
NO molecule contains rectangular dimers in the solid state.

5. Dinitrogen Trioxide, N_2O_3.

Since in liquid and gaseous states N_2O_3 dissociates to give NO and NO_2 as shown below :

$$N_2O_3 \rightleftharpoons NO + NO_2,$$

it may be assumed that N_2O_3 has the structure :



$$:\ddot{O}=\overset{\times\times}{N}-\underset{\cdot\cdot}{\ddot{O}}-\overset{\times\times}{N}=\ddot{O}: \quad or \quad ON{-}NO_2$$

This structure is confirmed by the tracer studies which have shown that when nitrogen dioxide labelled with N^{15} ($N^{15}O_2$) is mixed with $N^{14}O$, a rapid exchange between N^{14} and N^{15} atoms takes place as shown below :

$$N^{14}O + N^{15}O_2 \rightleftarrows N^{15}O + N^{14}O_2$$

N_2O_3 molecule is *diamagnetic* in spite of its intense blue colour and hence it is not an *odd electron molecule.*

4. Nitrogen Dioxide (NO_2) and Dinitrogen Tetroxide (N_2O_4).

NO_2 molecule has *V-shaped* structure with O—N—O bond angle = 132° and N—O distance = 1.19A° [Fig. 32.4(*a*)]. This structure shows that NO_2 has one unpaired electron and hence it is *an odd electron molecule*. Thus NO_2 is *paramagnetic*. NO_2 molecule has a tendency to dimerise to colourless dimer N_2O_4 which is *planar* with long N—N bond = 1.75A° and O—N—O bond angle = 132° as shown in Fig. 32.4(*b*). The planar structure of N_2O_4 admits some δ+ charge on each nitrogen atom. The repulsion between the adjacent δ+ charges make N—N bond longer than a single bond.

The bond between the two nitrogen atoms in N_2O_4 is established by the two unpaired electrons residing on nitrogen atom in NO_2. The structure of N_2O_4 as shown below shows that it has no unpaired electron and hence is *diamagnetic.* Note that NO_2 is paramagnetic.

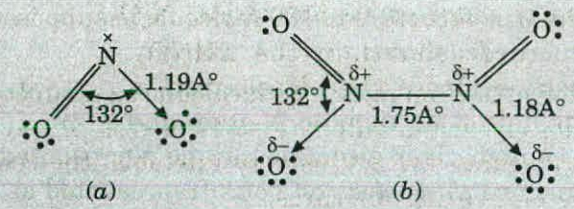
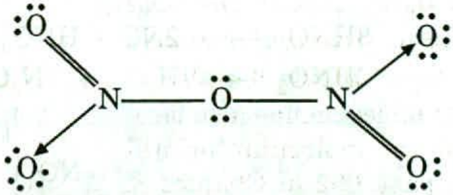


Fig. 32.4 (*a*) V-shaped structure of NO_2 molecule (*b*) Planar structure of N_2O_4 molecule.

5. Nitrogen Pentoxide, N_2O_5.

X-ray studies of N_2O_5 suggest that it is an ionic solid and hence is *nitronium nitrate*, $NO_2^+NO_3^-$. But in its vapour state it exists as a *symmetrical molecule* having the structure $O_2N—O—NO_2$ as shown below :



N—O—N bond is almost linear *i.e.* N—O—N bond angle = 80°.

Oxyacids

1. Hyponitrous Acid, HNO or $H_2N_2O_2$.

Preparation. Free acid is prepared by treating silver hyponitrite. $Ag_2N_2O_2$ with a solution of HCl in dry ether or with H_2S.

$$Ag_2N_2O_2 + 2HCl \longrightarrow \underset{\text{solution}}{H_2N_2O_2} + \underset{\text{ppt.}}{2AgCl}$$

$$Ag_2N_2O_2 + H_2S \longrightarrow \underset{\text{solution}}{H_2N_2O_2} + \underset{\text{ppt.}}{Ag_2S}$$

The solution containing $H_2N_2O_2$ is evaporated to dryness in vacuum when hygroscopic crystals (white leaflets when pure) of the acid are obtained.

Properties. Pure acid forms white leaflets which explode when rubbed. When exposed to air, the acid decomposes slowly giving HNO_2 and HNO_3 The aqueous solution of the acid decomposes on heating evolving N_2O.

$$2H_2N_2O_2 + 3O_2 \longrightarrow 2HNO_2 + 2HNO_3$$

$$H_2N_2O_2 \longrightarrow N_2O + H_2O$$

The acid is soluble in water, alcohol, chloroform, ether and benzene. It is a weak dibasic acid and hence forms two types of salts *viz.*, *acid salts* like $Ba(HN_2O_2)_2$ and *normal salts* (called *hyponitrites* like BaN_2O_2. The acid is a reducing agent and is oxidised to nitrate by acidified $KMnO_4$.

$$5H_2N_2O_2 + 8KMnO_4 + 12H_2SO_4 \longrightarrow 10HNO_3 + 4K_2SO_4 + 8MnSO_4 + 12H_2O$$

2. Nitrous Acid, HNO_2.

Preparation. This is an unstable acid and is known only in solution. A solution of nitrous acid may be prepared :

(*i*) by the action of water on its anhydride, N_2O_3.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

(*ii*) by the action of barium nitrite with calculated quantity of dilute sulphuric acid. The precipitate of barium sulphate so formed is filtred off and the filtrate contains nitrous acid. Since the acid is very unstable, the reaction is carried out at the temperature of freezing mixtures.

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow \underset{\text{ppt.}}{BaSO_4} + 2HNO_2$$

Properties. (*i*) Nitrous acid is a weak acid. Aqueous solution of nitrous acid is pale blue due to the presence of nitrogen trioxide. This colour fades on standing for some time. The acid is unstable and even in cold solution undergoes auto-oxidation. At higher temperatures it decomposes into nitric oxide and nitrogen peroxide.

$$\begin{array}{l} 3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O \\ 2HNO_2 \longrightarrow H_2O \;+\; \underset{\substack{\upharpoonleft\downharpoonright \\ NO + NO_2}}{N_2O_3} \end{array}$$

(*ii*) It acts as a good oxidising agent on account of the ease with which it can part with an atom of oxygen.

$$2HNO_2 \longrightarrow 2NO + H_2O + O$$

For example : (*a*) *It oxidised hydrogen sulphide to sulphur*

$$2HNO_2 + H_2S \longrightarrow 2H_2O + 2NO + S$$

(*b*) *Iodine is liberated from potassium iodide.*

$$2KI + 2HNO_2 \longrightarrow 2KOH + I_2 + 2NO$$

(*c*) *Stannous chloride is oxidised to stannic chloride.*

$$SnCl_2 + 2HCl + 2HNO_2 \longrightarrow SnCl_4 + 2NO + 2H_2O$$

(*d*) *It can oxidise sulpur dioxide to sulphuric acid.*

$$2HNO_2 + SO_2 \longrightarrow 2NO + H_2SO_4$$

(*e*) It can oxidise $FeSO_4$ to $Fe_2\,(SO_4)_3$

$$2FeSO_4 + H_2SO_4 + 4HNO_2 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$$

(*f*) *Hydriodic acid is oxidised to iodine.*

$$2HI + 3HNO_2 \longrightarrow I_2 + 2NO + 2H_2O$$

(*g*) *Sodium arsenite is oxidised to sodium arsenate.*

$$Na_3AsO_3 + 2HNO_2 \longrightarrow H_2O + 2NO + Na_3AsO_4$$

(*iii*) It can be easily oxidised to nitric acid and as such reduces strong oxidising agents.

$$HNO_2 + O \longrightarrow HNO_3$$

For example :

(*a*) *It reduces bromine and iodine to hydrobromic acid and hydriodic acid respectively.*

$$\begin{array}{l} HNO_2 + I_2 + H_2O \longrightarrow 2HI + HNO_3 \\ HNO_2 + Br_2 + H_2O \longrightarrow 2HBr + HNO_3 \end{array}$$

(*b*) *Acidified potassium permanganate is reduced to manganese sulphate*

$$KMnO_4 + 3H_2SO_4 + 5HNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$$

(*c*) *Acidified potassium dichromate is reduced to chromium sulphate (green colour).*

$$K_2Cr_2O_7 + 4H_2SO_4 + 5HNO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3HNO_3 + 4H_2O$$

(*d*) *It also reduces hydrogen peroxide*

$$H_2O_2 + HNO_2 \longrightarrow HNO_3 + H_2O$$

(*iv*) Nitrous acid reacts with alkalies to form nitrites. Nitrites are much more stable than nitrous acid.

$$NaOH + HNO_2 \longrightarrow NaNO_2 + H_2O$$

Uses. Nitrous acid is used in organic chemistry especially in the preparation of diazo compounds which are the basic substances in the manufacture of aniline dyes. It is also used both as an oxidising and reducing agent in analytical chemistry.

3. Nitric Acid, HNO_3.

In the laboratory it is prepared by heating conc. H_2SO_4 and an alkali nitrate in a glass retort.

Manufacture. (*i*) *From nitre ($NaNO_3$).* Nitric acid is prepared on a large scale by heating sodium nitrate with concentrated sulphuric acid. The mixture is placed in a cast iron retort (Fig. 32.5) and subjected to distillation at a temperature of about 200°C.

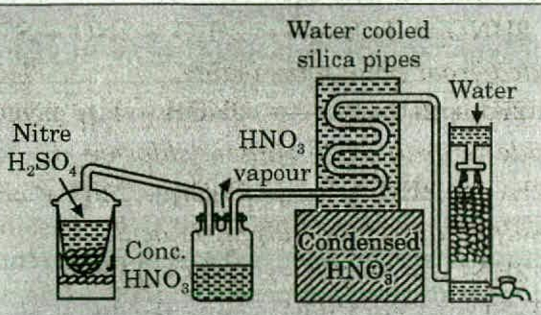


Fig. 32.5. Manufacture of nitric acid from nitre, $NaNO_3$.

The vapours of nitric acid from the pot are conducted to a trap and then passed through water-cooled silica pipes. The acid condensed in the pipes is sent back to the trap. The uncondensed vapours of nitric acid are then finally passed up a tower packed with quartz from the top of which a steam of water is trickling down. The vapours are dissolved in water and the dilute nitric acid thus produced collects at the bottom.

The residue left in the pot is known as *nitre cake* and is used in bleaching and dyeing industries. It is also used for the preparation of hydrochloric acid.

The acid so obtained is *concentrated* by distilling the dilute acid with concentrated sulphuric acids. Commercial nitric acid contains hydrochloric acid, sulphuric acid, iodine, iron salts and nitrogen pentoxide as impurities. A current of dry air passed through the liquid removes N_2O_5. Further *purification* is carried out by distilling the acid under reduced pressure.

(ii) From air by Birkland-Eyde process. Nitrogen and oxygen of the air combine to form nitric oxide when air is passed through an electric arc.

$$N_2 + O_2 \rightleftarrows 2NO - 43{,}200 \text{ cals.}$$

The reaction is endothermic and is favoured by a high temperature.

In the Birkland-Eyde process, air is blown into an electric arc struck between two water cooled copper electrodes and spread into a large disc with the help of a strong magnetic field applied at right angles (Fig. 32.6)

The issuing gases contain about 1.25 per cent of nitric oxide. The gases escaping from the furnace have to be rapidly cooled down to a temperature of about 1000°C. Their heat is used for steam raising.

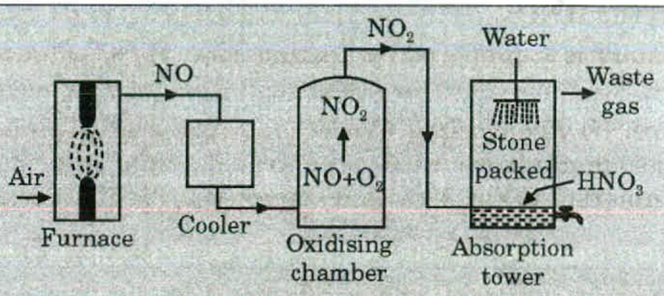


Fig. 32.6. Manufacture of nitric acid from air by Birkland-Eyde process.

At 600°C the nitric oxide begins to combine with oxygen to from nitrogen peroxide.

$$2NO + O_2 \rightleftarrows 2NO_2.$$

The oxides of nitrogen, after cooling to 50°C by passing the pipe through water boiler pass into a chamber lined with acid-proof stone in order to carry further the conversion into nitrogen peroxide. The oxide is then absorbed in water trickling over quartz stone in towers about 70 ft. high and 20 ft. in diameter.

The nitric acid in the tower reaches a strength of 30 to 40 per cent while in the succeeding towers, the strength remains at 20, 10 and 5 per cent respectively. In case of cold dilute solutions, the nitric acid is formed according to the equation

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

In the hot state, the nitrous acid under goes autoxidation to nitric acid, and the nitric oxide formed again takes up oxygen and forms nitrogen peroxide.

$$\begin{array}{rcl} 2HNO_2 & \longrightarrow & H_2O + 2NO + O \\ HNO_2 + O & \longrightarrow & HNO_3 \\ \hline 3HNO_2 & \longrightarrow & HNO_3 + 2NO + H_2O \end{array}$$

(iii) By catalytic oxidation of ammonia (Ostwald's process). Owing to the great wear and tear of the plant because of high temperature employed in the Birkland-Eyde process, Ostwald's process is finding preference.

In this method a mixture of ammonia gas with air in the ratio 1 : 8 is passed through a catalyst chamber packed with platinum gauze maintained at a temperature of 803°C. The ammonia is oxidised under these conditions to nitric oxide.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

The nitric oxide so formed is led to an oxidising tower (Fig. 32.7) where it combines with oxygen of the air to form nitrogen peroxide, NO_2

$$\underset{\text{Nitric oxide}}{2NO} + O_2 \longrightarrow \underset{\text{Nitrogen peroxide}}{2NO_2}$$

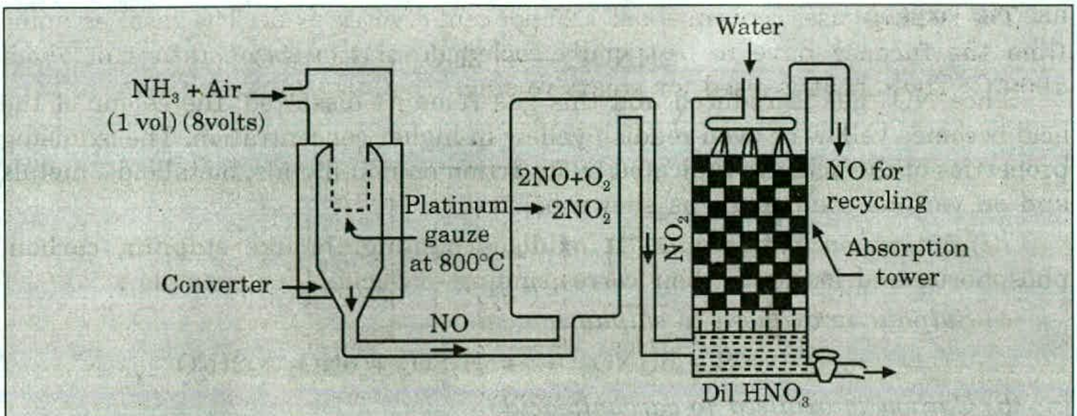


Fig. 32.7. Ostwald's process for the manufacture of nitric acid.

The resulting gas passes up a tower (called *absorption tower*) packed with earthen balls down which a spray of water trickles. Nitrogen peroxide reacts with water in the presence of oxygen forming nitric acid.

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

The acid so obtained is dilute and concentrated by distillation under reduced pressure.

Preparation of concentrated nitric acid. The dilute HNO_3 can be concentrated to 68% by distillation, when constant boiling mixture is formed. This constant boiling mixture of HNO_3 has a specific gravity of 1.42 and is the commercial concentrated HNO_3. More concentrated acid needed for certain uses such as nitration is produced by distillation with conc. H_2SO_4 which holds back the water. The distillate is 98% HNO_3. The cent percent HNO_3 is obtained by strongly cooling 98% acid when the pure acid is deposited as colourless crystals at –42°C. These crystals are separated and melted to 100% HNO_3.

A recently developed method for the direct production of conc. HNO_3 involves the reaction between the liquid NO_2 and water (or dil. HNO_3) in the presence of O_2 at 50 atm. pressure and a temperature of 75°C. The product is 88% HNO_3.

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

Preparation of fuming nitric acid. It is made by distilling conc. HNO_3 with a little starch. The starch reduces some acid to NO_2 which dissolves in the remaining acid to form fuming nitric acid. This acid is yellow in colour due to the presence in it of dissolved oxides of nitrogen highly corrosive liquid consisting of HNO_3. Fuming nitric acid is a much more powerful oxidising agent and nitrating agent than conc. HNO_3.

Physical properties of nitric acid. Pure HNO_3 is a colourless liquid with a characteristic choking smell. It boils at 86°C and freezes at –42°C into a transparent crystalline mass. It is soluble in water in all proportions. In the moist air, it fumes as its vapours form a mist of minute droplets of aqueous HNO_3.

Chemical properties of HNO_3 (1) **Oxidising property.** Nitric acid is a strong oxidising agent because of the ease with which it decomposes to give nascent oxygen.

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O$$

Since NO_2 gas is reduced and this gas remains dissolved, the colour of the acid becomes yellow or oven reddish yellow in higher concentration. The oxidising properties of the acid are indicated by its action on non-metals, metalloids, metals and on various compounds as shown below :

(*i*) *Action on non-metals.* It oxidises non-metals like sulphur, carbon, phosphorus and iodine to their corresponding oxy-acids. For example :

(*a*) *Sulphur is oxidised to sulphuric acid.*

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

(*b*) *Carbon is oxidised to carbonic acid.*

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + H_2O$$

(*c*) *Iodine is oxidised to iodic acid (HIO_3).*

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

(*d*) *Phosphorus is oxidised to ortho-phosphoric acid (H_3PO_4).*

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$

(*ii*) *Action on metalloids.* Metalloids like arsenic and antimony are oxidised to the corresponding oxy-acids. *e.g.*, arsenic is oxidised to ortho-arsenic acid (H_3AsO_4).

$$As + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$$

(*iii*) *Action on metals.* Most of the metals, with the exception of noble metals like gold and platinum, are attacked by nitric acid. Some like tin and antimony give *oxides* whilst the others form nitrates. During the reaction, a part of the acid is reduced to give products like NO_2, NO, N_2, N_2O, NH_2OH or NH_3 and the nature of products depends upon the concentration of the acid, temperature and the nature of the metal.

It is believed that the *primary reaction* in each case is the liberation of nascent hydrogen which then reduces the acid to different reaction products mentioned above.

$$M + HNO_3 \longrightarrow MNO_3 + H$$

According to another view, this reduction occurs only in case of metals which are above hydrogen in the electrochemical series. Metals like Cu, Ag, Hg which cannot displace hydrogen are oxidised by nitric acid and the oxide formed, being more basic, reacts with more of nitric acid to form the nitrate. Examples are :

(*a*) *Copper.* With dilute nitric acid, it gives nitric oxide.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

With concentrated nitric acid, it forms nitrogen peroxide.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Silver, mercury and lead give similar reactions.

(*b*) *Tin.* With dilute nitric acid, it forms stannous nitrate and ammonium nitrate.

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$$

With concentrated nitric acid it gives meta-stannic acid and nitrogen peroxide (*cf.* Action on non-metals).

$$Sn + 4HNO_3 \longrightarrow \underset{\text{Meta stannic acid}}{H_3SnO_3} + H_2O + 4NO_2$$

(*c*) *Zinc.* With very dilute nitric acid it gives ammonium nitrate.

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$$

With dilute acid, it produces N_2O while concentrated acid gives NO_2.

(*d*) *Magnesium and manganese* are the only metals that liberate hydrogen from dilute acid.

$$\underset{\text{dilute}}{2HNO_3} + Mg \longrightarrow Mg(NO_3)_2 + H_2$$

(*e*) *Gold* and *platinum* dissolve in a mixture of 1 part HNO_3 and 3 parts HCl known as *aqua regia*. The dissolution occurs as a result of the action of nascent chlorine on the metals.

$$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2Cl$$

(*iv*) *Action on compounds.* A number of compounds are oxidised. For example it oxidises :

(*a*) *sulphur dioxide to the sulphuric acid.*

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

(*b*) *sulphuretted hydrogen to sulphur.*

$$H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + S$$

(*c*) *ferrous sulphate to ferric sulphate* in the presence of sulphuric acid.

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

The nitric oxide formed gives a dark brown ring (*Ring test for nitrates*).

(*d*) *cane sugar to oxalic acid.*

$$C_{12}H_{22}O_{11} + 18O \longrightarrow 6(COOH)_2 + 5H_2O$$

(2) **Nitrating property.** It reacts with organic compounds and forms their nitro compounds. The reaction takes place in the presence of stronger acids like conc. H_2SO_4.

In the presence of an acid which is stronger than nitric acid, NO_2^+ ions (*nitronium ions*) are produced.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

When NO_2^+ ions replace the hydrogen ions in organic compounds, nitration is said to take place. Thus :

$$\underset{\text{benzene}}{C_6H_6} + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{nitrobenzene}}{C_6H_5NO_2} + H_2O$$

The yellow strain produced on wood or skin is due to this reaction.

(3) **Action on HCl.** A mixture of conc. HCl and conc. HNO_3 (3 : 1) is called aqua regia. It reacts considerably more vigorously than either of these acids taken separately.

$$HNO_3 + 3HCl \longrightarrow 2H_2O + \underset{\substack{\text{Nitrosyl} \\ \text{chloride}}}{NOCl} + Cl_2$$

Aqua regia dissolves even noble metals like gold and platinum.

$$Au + HNO_3 + 3HCl \longrightarrow AuCl_3 + NO + 2H_2O$$
$$3Pt + 4HNO_3 + 12HCl \longrightarrow 3PtCl_4 + 4NO + 8H_2O$$

The cause of greater activity of aqua regia is the formation of nascent chlorine at the moment of formation.

(4) **Acidic property.** Nitric acid is a strong acid. It ionises in aqueous solution as :

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

It decomposes metallic oxides, carbonates, bicarbonates, sulphides, sulphites, bisulphites and hydroxides forming metal nitrates. H_2S liberated in reaction between HNO_3 and a sulphide further reacts with HNO_3 to give sulphur.

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$
$$Na_2CO_3 + HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$
$$NaHCO_2 + HNO_3 \longrightarrow NaNO_3 + H_2O + CO_2$$
$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S$$
$$H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + S$$
$$NaSO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + SO_2$$
$$NaHSO_3 + HNO_3 \longrightarrow NaNO_3 + H_2O + SO_2$$
$$KOH + HNO_3 \longrightarrow KNO_3 + H_2O$$

Uses. It is used : (*i*) in the manufacture of *nitrates* which are important chemicals of commerce. Basic calcium nitrate is used as a fertilizer. Silver nitrate is used in photography and sodium nitrate in the manufacture of gun powder and fireworks. (*ii*) in the manufacture of *explosives* like nitroglycerine, dynamite, trinitrotoluene (T.N.T.), picric acid etc. (*iii*) in the manufacture of artificial silk, dyes, medicines and perfumes. (*iv*) in the purification of gold and silver. (*v*) as an important reagent in the laboratory. (*vi*) in the manufacture of H_2SO_4. (*vii*) in etching designs on wares of brass, bronze, etc. (*viii*) in the preparation of aqua regia.

4. Pernitric Acid, HNO_4.

It is prepared by dissolving N_2O_5 in anhydrous H_2O_2.

$$N_2O_5 + H_2O_2 \longrightarrow HNO_4 + HNO_3$$

It is unstable and explosive. It smells like bleaching powder. It is a powerful oxidising agent and oxidises aniline to nitrobenzene and liberates Br_2 from KBr solution.

Structure of Oxyacids

1. Hyponitrous Acid ($H_2N_2O_2$) and Hyponitrite Ion ($N_2O_2^{2-}$).

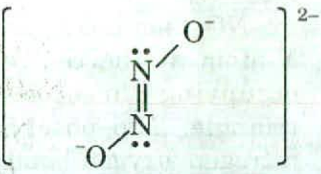
The molecular formula of the acid has been determined by the freezing point method. Because of the decomposition of its aqueous solution on heating into nitrous oxide, N_2O, and decomposition of its salts and esters on heating, giving N_2 as shown below :

$$H_2N_2O_2 \longrightarrow N_2O + H_2O$$
$$3Na_2N_2O_2 \longrightarrow 2NaNO_2 + 2Na_2O + 2N_2$$
$$(C_2H_5)_2N_2O_2 \longrightarrow C_2H_5OH + CH_3CH + N_2,$$

the acid is said to contain an azo group, —N = N— and hence is assigned the structure, HO—N = N—OH. Since this structure involves a double bond, *cis-trans* isomerism may be expected for this molecule. Thus the acid may have either of the following two structures :

cis-structure *trans*-structure

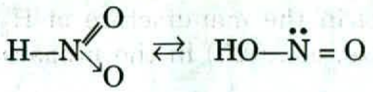
The value of dipole moment of the diethyl ester, $(C_2H_5)_2N_2O_2$ has been found to be equal to zero, showing that the acid has *trans* structure. Thus the *trans* structure of hyponitrite ion ($N_2O_2^{2-}$) can be shown as given in the margin. The *trans* structure of $N_2O_2^{2-}$ ion as given has also been confirmed by the infra-red spectra of sodium, mercury and silver salts of the acid.



trans structure of $N_2O_2^{2-}$ ion

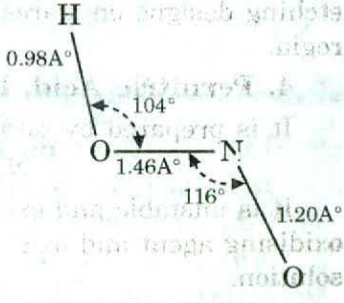
2. Nitrous Acid (HNO_2) and Nitrite Ion (NO_2^-).

When ethyl bromide, C_2H_5Br is distilled with $AgNO_2$, a mixture consisting of ethyl nitrite, C_2H_5—ONO and nitro ethane, $C_2H_5NO_2$ is obtained. The formation of these two compounds shows that nitrous acid forms two types of organic derivatives *viz.*, nitrites (*e.g.* C_2H_5—ONO) and nitro, compounds (*e.g.* C_2H_5—NO_2). On the basis of these two types of organic derivatives, nitrous acid is supposed to be an equilibrium mixture of the following two tautomeric forms :



There is, however, no physical evidence supporting the above view. Rather it is against it.

L.H. Jones, from an infra-red study of nitrous acid vapour (1951), came to the conclusion that the acid has a *trans* configuration with the dimensions shown in the margin.



Structure of HNO_2 acid

X-ray and Raman studies of crystalline $AgNO_2$ and $NaNO_2$ have shown that NO_2^- ion has an angular structure [Fig. 32.8(*a*)] with ONO bond angle and N—O bond length equal to 116° or 182° and 1.13 Å or 1.23 Å respectively. These two sets of results have been reported by different workers. The discrepancy has not yet been explained. Since nitrogen–oxygen bonds in NO_2^- ion are equivalent, the ion is said to be a resonance hybrid of the two structures shown at (*b*) and (c) of Fig. 32.8.

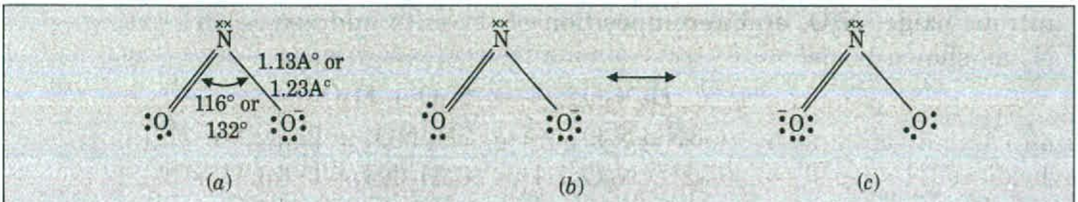


Fig. 32.8. (*a*) Angular structure of NO_2^- ion. (*b*) and (c) NO_2^- ion is said to be a resonance hybrid of these two structures.

3. Nitric Acid (HNO_3) and Nitrate Ion (NO_3^-).

HNO_3 is a monobasic acid and can be represented as $HO—\underset{\underset{O}{\downarrow}}{N}=O$. As indicated by electron diffraction studies, the molecule of nitric acid, *in the vapour state*, possesses a planar structure shown in Fig. 32.9.

NO_3^- ion has *trigonal planar geometry* with N-atom at the centre and three O-atoms are occupying three corners of the equilateral triangle. The observed bond length of each nitrogen–oxygen bond is 1.21 Å and each ONO bond angle is equal to 120°. The triangular planar geometry of NO_3^- ion results from sp^2 hybridisation of N-atom. Since the observed nitrogen–oxygen bond length (= 1.21Å) is intermediate between the calculated N—O (= 1.36 Å) and N = O (= 1.15Å) bond lengths, the actual structure of NO_3^- ion is supposed to be a resonance hybrid of various resonating structures.

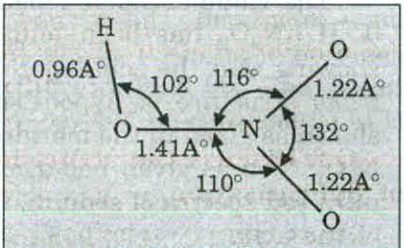


Fig. 34.9. Structure of HNO_3 molecule in the vapour state.

4. Pernitric Acid, HNO_4.

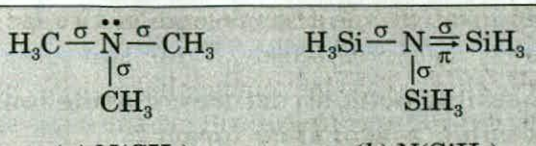
Like HNO_3. HNO_4 also has a simple structure which is represented as $O=\underset{\underset{O}{\downarrow}}{N}—O—OH$.

Questions with Answers

[A] Questions on Hydrides of Nitrogen.

Q.1 Discuss the structers of trimethylamine, $N(CH_3)_3$ and trisilylamine, $N(SiH_3)_3$ molecules.

Ans : The structure of $N(CH_3)_3$ and $N(SiH_3)_3$ molecules are given at (*a*) and (*b*) respectively of Fig. 32.10.



$$\mathrm{H_3C} \overset{\sigma}{-} \underset{\underset{\mathrm{CH_3}}{|\sigma}}{\ddot{\mathrm{N}}} \overset{\sigma}{-} \mathrm{CH_3} \qquad \mathrm{H_3Si} \overset{\sigma}{-} \underset{\underset{\mathrm{SiH_3}}{|\sigma}}{\mathrm{N}} \overset{\sigma}{\underset{\pi}{=}} \mathrm{SiH_3}$$

(*a*) $N(CH_3)_3$ (*b*) $N(SiH_3)_3$

Fig. 32.10 Structure of (*a*) trimethylamine molecule, $N(CH_3)_3$ and (*b*) trisilylamine molecule, $N(SiH_3)_3$.

Structure of $N(CH_3)_3$ molecule shown at (*a*) shows that since N-atom (central atom) is surrounding by three σ-*bps* and one *lp* of electrons, this atom is sp^3 hybridised [$N = (sp^3)^1 (sp^3)^1 (sp^3)^1 (sp^3)^2$]. Due to sp^3 hybridistion and the presence of one *lp* of electrons in one of the four sp^3 hybrid orbitals, $N(CH_3)_3$ molecule has **trigonal pyramidal shape**.

The structure of $N(SiH_3)_3$ molecule shown at (*b*) shows that since N-atom (central atom) is surrounded by *three* σ-*bps* and *no lp of electrons*, this atom is sp^2 hybridised [$N \rightarrow (sp^2)^1 (sp^2)^1 (sp^2)^1 2p^2$].

The presence of π bond [$(N \rightarrow Si)\pi$ bond] has no effect on sp^2 hybridsation. In sp^2 hybridsation one $2p$ orbital which contains one electron pair remains unhybridised. The electron pair present in $2p$ orbital of N-atom is donated to the vacant $3d$ orbiatl of Si-atom ($Si = 3s^2\ 3p^2\ 3d^\circ = 3s^1\ 3p^1\ 3p^1\ 3p^1\ 3d^\circ$) to form $(p\pi - d\pi)\pi$ bond. This π bond is represented as $[2p^2\ (N) \rightarrow 3d^\circ\ (Si)]\pi$ bond. The donation of an electron pair from the filled $2p$ orbital to the vacant $3d$ orbital is called **($p\pi - d\pi$) back bounding.** Due to sp^2 hybridisation of N-atom and absence of *lp* of electrons on N-atom, $N(SiH_3)_3$ molecule has **trigonal planar geometry**.

Q.2 Discuss the structure/geometry of amide ion (NH_2^-) on the basis of hybridisation.

Ans : Since N-atom has higher EN than H-atom, negative charge on NH_2^- ion can be assumed to be present on N-atom. Consequently structure of NH_2^- ion can be written as $\mathrm{H} - \overset{-}{\underset{\cdot\cdot}{\ddot{\mathrm{N}}}} - \mathrm{H}$. Since N-atom (central atom) is surrounded by σ-*bps* + *lps* = 2 + 2 = 4, N-atom is sp^3 hybridised as shown in Fig. 32.11.

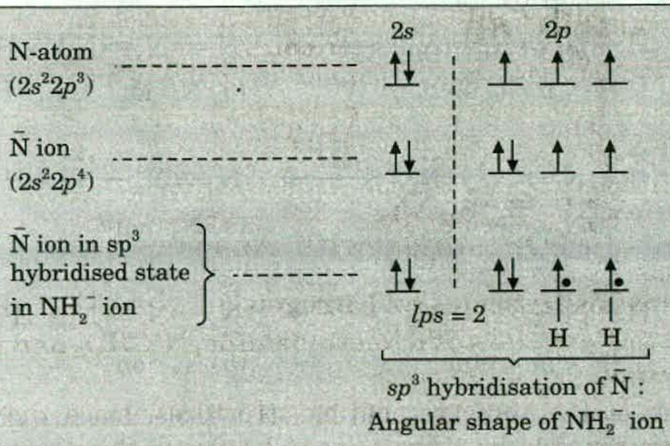
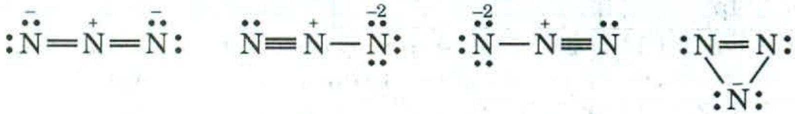


Fig 32.11 sp^3 hybridisation of N^- in NH_2^- ion.

Due to sp^3 hybridisation and the presence of two *lps* of electrons NH^-_2 ion has angular geometry.

Q.3 Draw all possible octet structures of azide ion, N_3^-. Which of these structures are possible reasonance forms ?

Ans : Possible structures of N_3^- ion satisfying octet rule (*i.e.* octet structures) can be written as :



$:\overset{-}{\ddot{N}}=\overset{+}{N}=\overset{-}{\ddot{N}}:$ $\quad N\equiv\overset{+}{N}-\overset{-2}{\ddot{\underset{..}{N}}}:$ $\quad :\overset{-2}{\ddot{\underset{..}{N}}}-\overset{+}{N}\equiv\ddot{N}$

(*a*) (*b*) (*c*) (*d*)

Structures (*a*), (*b*) and (*c*) have been obtained by removing H-atom from the structures of hydrazoic acid molecule (HN_3). Structure (*d*) is a ring structure. Ring structure (*d*) is ruled out because N_3^- ion has linear geometry. Besides the bond angle of 60° or less demanded by the ring structure requires considerable strain from the normal angles of bonding. This discussuin shows that structures (*a*), (*b*) and (*c*) are the only structures which can be called resonance froms of N_3^- ion, *i.e.* the true structure of N_3^- ion is a reasonance hybrid of structures (*a*), (*b*) and (*c*).

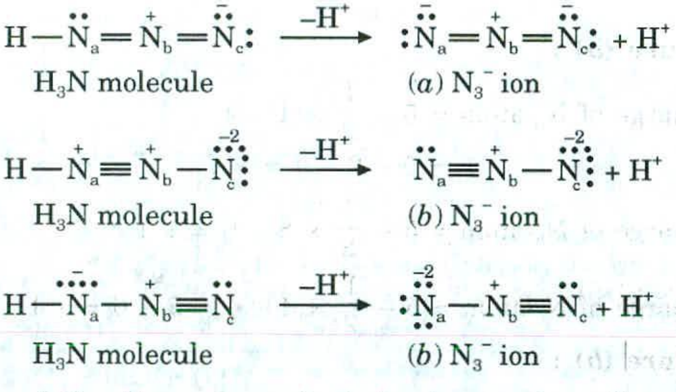
Q.4 (*i*) Write the three resonating octet structures of azide ion (N_3^-).

(*ii*) Explain the linear structure of N_3^- ion and formation of different bonds in it.

(*iii*) Determine the formal charge of each N-atom in each of the three structures of N_3^- ion.

(*iv*) The observed nitrogen-nitrogen bond length in N_3^- ion is 1.16A° which is shorter than the predicted value of 1.26A°. Explain.

Ans : (*i*) The resonating structures of N_3^- ion in which all the three N-atoms have an octet of electrons can be obtained by removing H-atom from the resonating structures of hydrazoic acid molecule, H_3N. In order to differentiate the three N-atoms they have been designated as N_a, N_b and N_c.



$$H-\ddot{N}_a=\overset{+}{N}_b=\ddot{N}_c: \xrightarrow{-H^+} :\overset{-}{\ddot{N}}_a=\overset{+}{N}_b=\overset{-}{\ddot{N}}_c: + H^+$$

H_3N molecule (*a*) N_3^- ion

$$H-\overset{+}{N}_a\equiv\overset{+}{N}_b-\overset{-2}{\ddot{N}}_c: \xrightarrow{-H^+} \ddot{N}_a\equiv\overset{+}{N}_b-\overset{-2}{\ddot{N}}_c: + H^+$$

H_3N molecule (*b*) N_3^- ion

$$H-\overset{-}{\ddot{N}}_a-\overset{+}{N}_b\equiv\ddot{N}_c \xrightarrow{-H^+} :\overset{-2}{\ddot{N}}_a-\overset{+}{N}_b\equiv\ddot{N}_c + H^+$$

H_3N molecule (*b*) N_3^- ion

(*ii*) In each of the three resonating structures, since the central N-atom (N_b^+ atom) is surrounded by σ-*bps* + *lps* = 2 + 0 = 2, this atom is *sp* hybridised. Due to *sp* hybridisation and absence of any *lp* of electrons on N_b^+ atom, N_3^- ion has linear geometry. The formation of differnt bonds in structure (*a*) has been shown in Fig. 32.12.

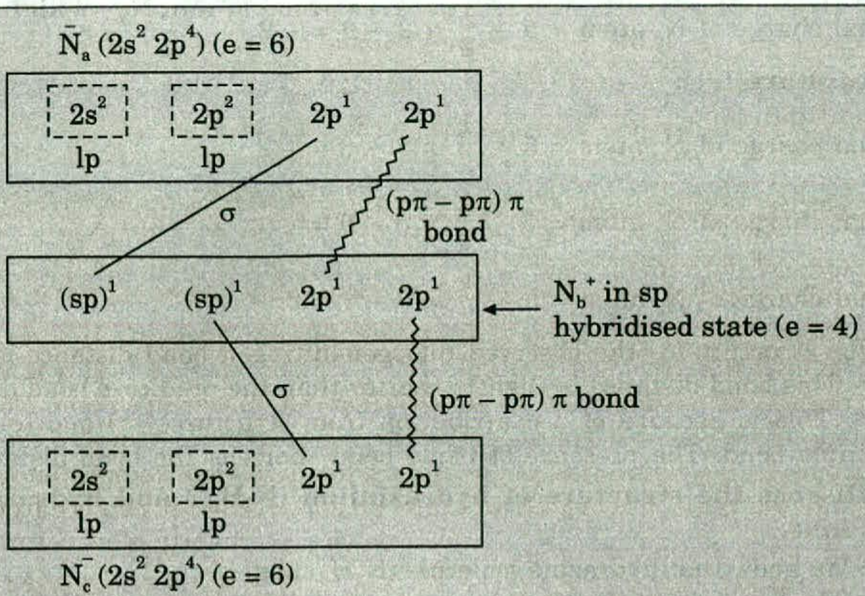


Fig. 32.12 Formation of different bonds in N_3^- ion having the structure $:\overset{-}{\ddot{N}}_a{=}\overset{+}{N}_b{=}\overset{-}{\ddot{N}}_c:$

(*iii*) We know that :

Formal charge of an atom in a given molecule

= No. of electrons present in the valence-shell of the atom $- \frac{1}{2}$ × No. of electrons shared by that atom with the neighbouring atom – No. of electrons from the lone pairs of electrons on the atom.

Thus :

In structure (*a*) :

Fromal charge of N_a-atom $= 5 - \frac{1}{2} \times 4 - 4$

$= 5 - 2 - 4 = -1$

Fromal charge of N_b-atom $= 5 - \frac{1}{2} \times 8 - 0 = +1$

Formal charge of N_c-atom $= 5 - \frac{1}{2} \times 4 - 4 = 5 - 6 = -1$

In structure (*b*) :

Formal charge of N_a-atom $= 5 - \frac{1}{2} \times 6 - 2 = 0$

Formal charge of N_b-atom $= 5 - \frac{1}{2} \times 8 - 0 = +1$

Formal charge of N_c-atom $= 5 - \frac{1}{2} \times 2 - 6 = -2$

In sturcture (*c*) :

Fromal charge of N_a-atom $= 5 - \frac{1}{2} \times 2 - 6 = -2$

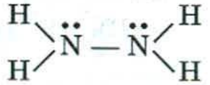
Formal charge of N_b-atom $= 5 - \frac{1}{2} \times 8 - 0 = +1$

Formal charge of N_c-atom $= 5 - \frac{1}{2} \times 6 - 2 = 0$

(*iv*) For structure (*a*) the observed nitrogen–nitrogen bond distance is equal to 1.16A°. This bond distance is slightly shorter than the predicted bond distance of 1.26A°. This is because of a contribution from structures (*b*) and (*c*) which contain triple bond. The presence of triple bond shortens the bond distance.

Q.5 Discuss the structure of hydrazinium ($N_2H_5^+$) and hydrazoinum ($N_2H_6^{2+}$) ions.

Ans : We know that hydrazine molecule (N_2H_4) has two *lps* of electrons on its two N-atoms as shown in its structure given in the margin. When one N-atom of N_2H_4 donates its *lp* of electrons to H^+ ion ($H^+ = 1s^\circ$), $N_2H_5^+$ ion is obtained. Similary when both N-atoms of N_2H_4 donate their *lp* of electrons to two H^+ ions, $N_2H_6^{2-}$ ion is obtained.



Structure of hydrazine molecule (N_2H_4)

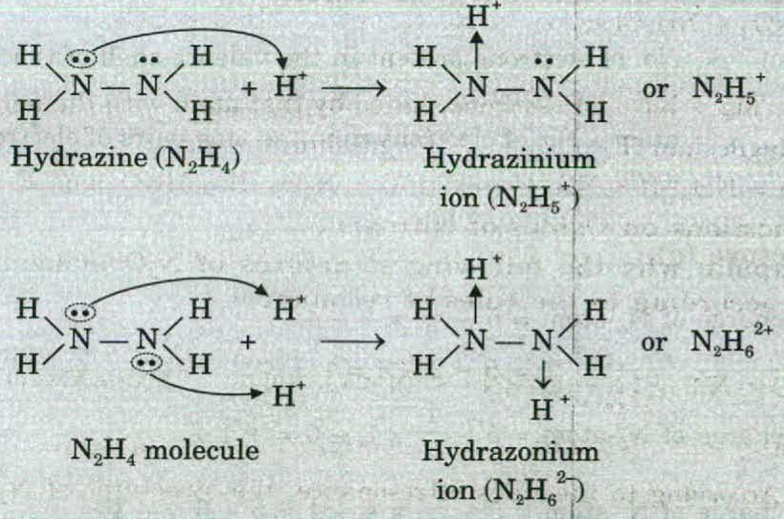
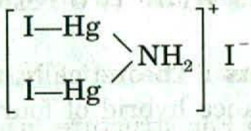


Fig. 32.13 Structures of $N_2H_5^+$ and $N_2H_6^{2+}$ ions

It may be seen from the structures of $N_2H_5^+$ and $N_2H_6^{2+}$ ions that each N-atom is sp^3 hybridise.

Q.6 Substance (A) is a colourless pungent smelling gas of vapour density 8.5. It turned Nessler's reagent brown (A) on oxidation at high temperature with platium catalyst gave a colurless gas (B), which readily turned brown in air, forming a gas (C). (B) and (C) were condensend together to give substance (D), which reacted with water to form an acid (E). When (E) was heated with a solution of NH_4Cl, a stable gas (F) was evolved. (F) did not support combustion, but magnesium continued to burn in it. Identity substences (A) to (F) and explain all the reactions involved.



Ans : (*i*)
$$\underset{\text{Nessler's reagent}}{2K_2[HgI_4]} + \underset{\text{Ammonia (A)}}{2NH_3(g)} \longrightarrow 4KI + NH_4I + \underset{\text{Iodide of Millon's base (Brown ppt)}}{\left[\begin{array}{l} I\text{—}Hg \\ I\text{—}Hg \end{array}\!\!\!\!\!\!\!\!\!\!>NH_2\right]^{+} I^{-}}$$

(*ii*)
$$\underset{\text{Ammonia (A)}}{4NH_3} + 5O_2 \xrightarrow{\text{Pt. Heat}} \underset{\text{Nitric oxide (B)}}{4NO} + 6H_2O$$

(*iii*)
$$\underset{\text{(B)}}{2NO + O_2} \longrightarrow \underset{\substack{\text{Nitrogen dioxide (C)} \\ (Brown)}}{2NO_2}$$

(*iv*)
$$\underset{\text{(B)}}{NO} + \underset{\text{(C)}}{NO_2} \xrightarrow{\text{Condensed}} \underset{\text{Dinitrogen trioxide (D)}}{N_2O_3}$$

(*v*)
$$\underset{\text{(D)}}{N_2O_3} + H_2O \longrightarrow \underset{\text{Nitrous acid (E)}}{2HNO_2}$$

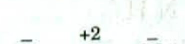
(*vi*)
$$\underset{\text{(E)}}{HNO_2} + NH_4Cl \longrightarrow \underset{\text{Nitrogen (F)}}{N_2} + 2H_2O + HCl$$

(*vii*)
$$\underset{\text{Magnesium (F)}}{Mg + N_2} \xrightarrow{\text{Heat}} \underset{\text{Magnesium nitride}}{Mg_3N_2}$$

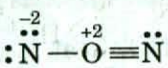
Thus A = NH_3, B = NO, C = NO_2, D = N_2O_3, E = HNO_2 and F = N_2.

[B] Questions on Oxides of Nitrogen.

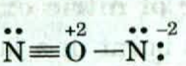
Q.1 Expalin why the following structures of N_2O molecule are not possible (according to the rules of resonance)



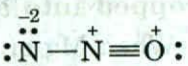
(a)



(b)



(c)



(d)

Ans : Accoridng to the rules of resonance, the structures of N_2O molecule given above are not possible. since in structure (*a*), (*b*) and (*c*) positive charge is present on the more electronegative O-atom and in structure (*d*), + + chrages (which are like chrages) are present on the adjacent N and O-atoms.

Q.2 Nitrous oxide (N_2O) supports combustion more vigrously than air. Explain.

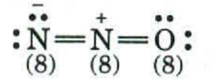
Ans : Nitrous oxide (N_2O) decomposes to give N_2 and O_2.

$$2N_2O \longrightarrow \underbrace{2N_2 + O_2}_{\substack{\text{Ratio} = 2\ :\ 1 \\ \text{Total volume} = 3}}$$

We know that O_2 present in air is 1/5 of the total volume of air while, as is evident from the above equation, O_2 produced by the decomposition of N_2O is 1/3 of the total volume of the gases mixture, ($N_2 + O_2$). It is due to the greater content of O_2, N_2O supports combustion more vigorously than air.

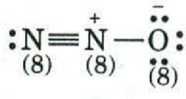
Q.3 Write two resonating structures of N_2O that satisfy octet rule. ***(I.I.T. 1985, 90; MLNR 1993)***

Ans : Theoretically, the true structure of N_2O molecule is supposed to be a resonance hybrid of four structures. All these structures obey octet rule. Out of these structures, two are covalent and two are ionic. Covalent structures donot contribute much to the actual structure of N_2O molecule. Thus we are left with only two ionic structures which contribute to real structure of N_2O. These two ionic structures are given below :



$$:\overset{-}{\ddot{\underset{(8)}{N}}}=\overset{+}{\underset{(8)}{N}}=\ddot{\underset{(8)}{O}}:$$

(I)



$$:\underset{(8)}{N}\equiv\overset{+}{\underset{(8)}{N}}-\overset{-}{\ddot{\underset{\ddot{(8)}}{O}}}:$$

(II)

Each atom in both the structures sutisfies octet rule.

Q.4 Nitric oxide is a netral oxide. Explain why ?

Ans : Nitric oxide (NO) is a netural oxide due to the following properties shown by NO.

(*i*) NO reacts neither with an acid nor with an alklali.

(*ii*) NO does not give any acid with water.

Q.5 Nitric oxide turns brown in air. Why ? ***(B.I.T. 1987)***

Ans : Nitric oxide (NO) (colourless) directly reacts with O_2 of the air and brown fumes of NO_2 are formed.

$$\underset{\text{(Colourless)}}{2NO} + O_2 \text{ (From air)} \longrightarrow \underset{\text{(Brown fumes)}}{2NO_2}$$

Q.6 Burning Mg continues to burn while burning S gets extingunished when dropped into a jar of nitric oxide.

Ans : When Mg or S is burnt in a jar of NO, heat is evolved. The quantity of heat produced during the buring of Mg is quite sufficient to decompose NO to N_2 and O_2 ($2NO \xrightarrow{\Delta} N_2 + O_2$). O_2 thus produced keeps Mg burning. On the other hand, the quantity of heat produced during the burning of S is not quite sufficient and NO does not get decompose to produce O_2. Due to the absence of O_2, S stops burning.

Q.7 Nitric oxide (NO) is paramagetic in the gaseous state but diamagnetic in the liquid and solid state. Expalin.

or Nitric oxide (NO), though an odd-electron molecule, is diamagnetic in the liquid state. Explain (I.I.T. 1991)

Ans : We know that in the gaseous state, nitric oxide exists as a monomeric molecule, NO. This monomeric molecule has one unpaired electron on N-atom ($:\dot{N}=\ddot{O}:$). It is due to the presence of one unpaired electron that NO molecule in the gaseous state shows paramagnetic character.

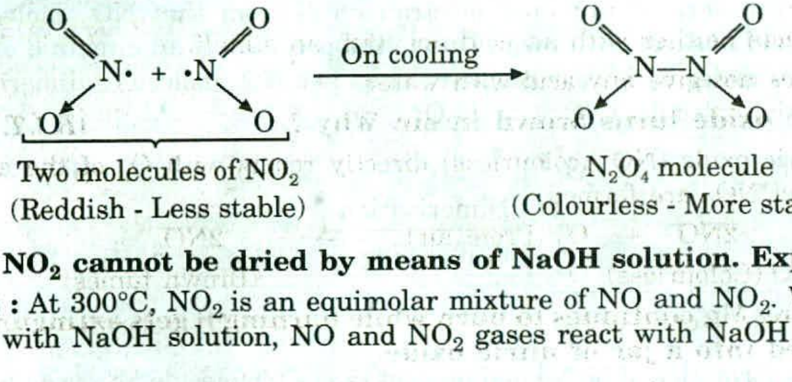
In the solid and liquid state, the monomeric NO molecule gets dimerised to form a symmetrical or asymmetrical dimer, $:\ddot{O}=\ddot{N}-\ddot{N}=\ddot{O}:$. This dimer is formed through the pairing of two unpaired electrons present on N-atoms of two NO molecules.

$$\underbrace{:\ddot{O}=\ddot{N}\cdot + \cdot\ddot{N}=\ddot{O}:}_{\text{Two NO molecules}} \xrightarrow{\text{Dimerisation}} \underset{\text{Dimer}}{:\ddot{O}=\ddot{N}-\ddot{N}=\ddot{O}:}$$

Since this dimer has all the electrons in the paired state, NO molecule in the solid and liquid state is diamagnetic.

Q.8 Reddish brown NO_2, on cooling undergoes dimerisation to give colourless dinitrogen tetraoxide, N_2O_4. Explain the change.

Ans : NO_2 molecule is an odd-electron molecule ($e = 5 + 6 \times 2 = 17$) and hence has one unpaired electron. Due to the presence of unpaired electron, NO_2 has colour (reddish brown). On cooling, NO_2 molecule gets dimerised and forms dinitrogen tetraoxide (N_2O_4) which contains one N–N bond. Due to the presence of N–N bond in N_2O_4, all the electrons in this molecule become paired and hence N_2O_4 is colourless.



Two molecules of NO_2 (Reddish - Less stable)

N_2O_4 molecule (Colourless - More stable)

Q.9 NO_2 cannot be dried by means of NaOH solution. Expalin why ?

Ans : At 300°C, NO_2 is an equimolar mixture of NO and NO_2. When NO_2 is treated with NaOH solution, NO and NO_2 gases react with NaOH and produce $NaNO_2$

$$NO_2 + NO + 2NaOH \rightarrow 2NaNO_2 + H_2O$$

Since NO_2 reacts with NaOH as shown above, this gas cannot be dried by NaOH.

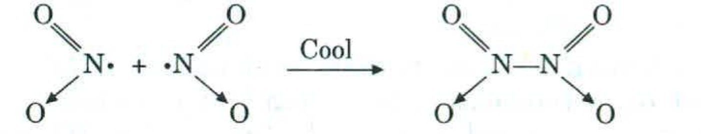
Q.10 Expalin why the following structure of NO_2 molecule is wrong ? $:\ddot{O}=\dot{N}=\ddot{O}:$.

Ans : Since nitrogen is an element of *2nd* period of the periodic table, it should have an octet of electrons in its valence shell. However, in the given structure N-atom has 4 + 4 + 1 = 9 electrons in its valence-shell which is beyond an octet.

Q.11 Althrough NO and NO_2 both contain one unpaired electron, yet NO does not dimerise while NO_2 is readily dimerised.

Ans : The structures of NO and NO_2 molecules show that both the molecules have one unpaired electron. In case of NO molecule the unpaired electron is not localised on a particular atom but is spread over the whole molecule while in NO_2 molecule the unpaired electron is localised on N-atom in its sp^2 hybrid orbital. Since in NO molecule the unpaired electron is spread over the whole molecule, there is a possibilty of the dimersation of two NO molecules to form an asymmetrical loose dimer in which N...O bond is a weaker bond.

In case of NO_2 molecule, since the unpaired electron is localised on N-atom, there is a possibility for the dimerisation of two monomeric NO_2 molecules to form the dimeric molecule, $(NO_2)_2$ or N_2O_4. The dimerisation (*i.e.* formation of N_2O_4 molecule) takes palce through the pairing of two unpaired electrons on two N-atoms of two NO_2 molecules.

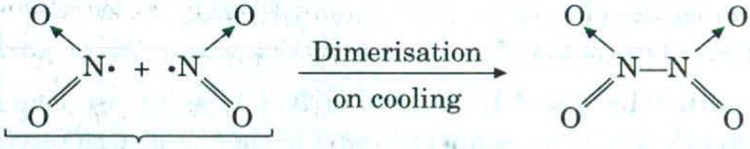


Two molecules of NO_2 Dinitrogen tetroxide (N_2O_4)

(*Monomers, less stable*) (*Dimer, more stable*)

Q.12 NO_2 is paramagnetic and brown gas but N_2O_4 is diamagnetic and colourless. Explain.

Ans : We know that NO_2 molecule has one unpaired electron on N-atom. It is due to the presence of unpaired electron on N-atom that NO_2 molecule is paramagnetic and has colour (brown). Due to the presence of an unpaired electron on N-atom, NO_2 molecule is very reactive. Thus two NO_2 molecules dimerise and give the dimeric molecule, $(NO_2)_2$ or N_2O_4.



Two molecules of NO_2 N_2O_4 molecule

Since in the formation of N–N bond present in N_2O_4 molecule, the two unpaired electrons residing on two N-atoms of two NO_2 molecules get paired, N_2O_4 molecule has all the electrons in the paired state and hence N_2O_4 molecule is diamagnetic and colourless.

Q.13 P_2O_5 is used in the preparation of N_2O_5 from HNO_3. Explain why ?

Ans : N_2O_5 is prepared by heating HNO_3 in presence of P_2O_5

$$2HNO_3 \xrightarrow[\text{of } P_2O_5]{\text{Heat in presence}} N_2O_5 + H_2O$$

In the above reaction, P_2O_5 is used since this oxide, being a strong dehydating agent, removes H_2O by reacting with it to form HPO_3 and H_3PO_4

$$H_2O + P_2O_5 \longrightarrow 2HPO_3, \quad 3H_2O + P_2O_5 \longrightarrow 2H_3PO_4$$

Q.14 Arrange the oxides of nitrogen in the increasing order of their acidic nature.

Ans : We know that oxides formed by N are : N_2O, NO, N_2O_3, NO_2 and N_2O_5. The acidic nature of these oxides increases with the increase of oxidation state (O.S.) of N-atom. Thus :

Oxides :	N_2O	NO	N_2O_3	NO_2	N_2O_5
O.S. of N :	+ 1	+ 2	+ 3	+ 4	+ 5

Increases ⟶

Acidic nature : Increases ⟶

Q.15 How would you distingnish among NO, N_2O_5 and NO_2.

Ans : NO is colourless gas which turns brown in air due to the oxidation of NO to NO_2

$$\underset{\text{Colourless gas}}{2NO} + O_2 \text{ (Form Air)} \longrightarrow \underset{\text{Brown gas}}{2NO_2}$$

N_2O_5 is a volatile solid which, due to its acidic nature, dissolves in H_2O with a hissing noise and gives HNO_3

NO_2 is a brown gas which condenses to a yellow liquid (N_2O_4) below – 20°C.

$$\underset{\text{Brown gas}}{2NO_2} \xrightarrow[\text{below } -20^\circ\text{C}]{\text{Condensation}} \underset{\text{Yellow liqiud}}{N_2O_4}$$

Q.16 A colourless inorganic salt (A) decomposes at about 250°C to give only two products, (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in the excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process. ***(I.I.T. 1996)***

Ans : Balanced equations for the reactions involved are :

$$\underset{\text{(A)}}{NH_4NO_3} \xrightarrow{250^\circ C} \underset{\substack{\text{Nitrons oxide-}\\ \text{gas-neutral}\\ \text{oxide (B)}}}{N_2O} + \underset{\substack{\text{Water-liquid-}\\ \text{neutral oxide}\\ \text{(C)}}}{2H_2O}$$

$$\underset{\substack{\text{White}\\ \text{phosphorus}}}{P_4} + \underset{\text{(B)}}{N_2O} \longrightarrow \underset{\substack{\text{Phosphorus}\\ \text{pentoxide (white}\\ \text{dehydrating agent)}}}{P_4O_{10}} + 10N_2$$

[C] Questions on Oxy acids of Nitrogen.

Q.1 Which has more acidic strength : HNO_2 or HNO_3 ?

Ans : HNO_3 has greater acidic strength (more acidic) than HNO_2. (HNO_3 > HNO_2)

Explanation. Higher acidic character of HNO_3 is due to higher O.S. of N-atom in HNO_3. ($H^{+5}NO_3 > H^{+3}NO_2$).

Q.2 HNO_3 acts only as an oxidising agent (O.A.) while HNO_2 can act both as an oxidising agent and reducing agent (R.A.). Explain why ? ***(Roorkee 1987)***

Ans : In HNO_3, N-atom is in + 5 oxidation state. + 5 oxidation state is the highest oxidation state exhibited by N-atom in its compounds. If HNO_3 acts as an O.A., this oxidation state of N-atom (= + 5) will be decreased. The decrease in O.S. is possible, since N-atom also shows oxidation states lower than + 5. If HNO_3 acts as a R.A., O.S. of + 5 of N-atom will be increased. The increase in O.S. of N-atom is not possible, since N-atom is not able to show an O.S. higher than +5. Thus HNO_3 can act only as an O.A.

In HNO_2, N-atom is in + 3 oxidation state. If HNO_2 acts as an O.A., the O.S. of N-atom (= + 3) will be decreased. The decrease in O.S. is possible , since N-atom also shows oxidation states lower than + 3. If HNO_2 acts as a R.A., the O.S. of N-atom (= + 3) will be increased. The increase in O.S. is also possible, since N-atom also exhibits oxidation states higher than + 3. Thus HNO_2 can act both as O.A. and as R.A.

Q.3 What happens when P_2O_5 reacts with conc. HNO_3 ?

Ans : Since P_2O_5 is a powerful dehydarting agent, it extracts water from HNO_3 and HNO_3 gets dehydarted resulting in the formation of N_2O_5.

$$2HNO_3 \xrightarrow[\text{of } P_2O_5]{\text{In presence}} H_2O + N_2O_5$$

Now since P_2O_5 has strong affinity for H_2O, it combines with H_2O lost by HNO_3 and forms metaphosphoric acid (HPO_3)

$$H_2O + P_2O_5 \longrightarrow 2HPO_3$$

On adding the above equation we get the final equation as :

$$2HNO_3 + P_2O_5 \longrightarrow N_2O_5 + 2HPO_3$$

Q.4 Fresh conc. HNO_3 is colourless but it turnes yellow on standing in sun light.

or Fresh conc. HNO_3 is colourless but old (*i.e.* commercial) sample of HNO_3 is yellow.

Ans : When conc. HNO_3 is allowed to stand in sunlight, it gets decomposed to give NO_2. NO_2 thus formed gets dissolved in HNO_3 and gives yellow colour to HNO_3

$$4HNO_3(l) \xrightarrow[\text{in sunlight}]{\text{Decomposition}} 4NO_2(g) + O_2(g) + 2H_2O(l)$$

HNO_3 containing dissolved NO_2 is called **fuming nitric acid.**

Q.5 Aluminium containers can be used for storing conc. HNO_3. Expalin why ?

Ans : In presence of conc. HNO_3, Al becomes passive due to the formation of a thin protective layer of its oxide (Al_2O_3) on its surface. This layer of Al_2O_3

prevents the further action of the acid on Al metal. Therefore, Al containers can be used for storing conc. HNO_3.

Q.6 Complete and balance the following equations in basic medium.

(*i*) $Al + NO_3^- \rightarrow Al(OH)_4^- + NH_3$

(*ii*) $Zn + NO_3^- \rightarrow ZnO_2^{2-} + NH_3$

Ans : (*i*) The given equation shows that Al (Al = 0) is being oxidised to $Al(OH)_4^-$ (Al = + 3) and NO_3^- ion (N = + 5) is being reduced to NH_3 (N = − 3). Thus reaction (*i*) in its complete/balanced form can be obtained by adding half-reactions (*a*) and (*b*) given below :

$$(a)\ \underset{(Al\,=\,0)}{Al} + 4OH^- \xrightarrow{\text{Oxidation}} \underset{(Al\,=\,+3)}{Al(OH)^-_4} + 3e^-\ ] \times 8$$

$$(b)\ \underset{(N\,=\,+5)}{NO_3^-} + 6H_2O + 8e^- \xrightarrow{\text{Reduction}} \underset{(N\,=\,-3)}{NH_3} + 9OH^-] \times 3$$

$$8Al + 3NO_3^- + 18H_2O + 5OH^- \longrightarrow 8Al(OH)_4^- + 3NH_3$$

(*ii*) The given equation shows that Zn (Zn = 0) is oxidised to ZnO_2^{2-} ion (Zn = + 2) and NO_3^- ion (N = + 5) is reduced to NH_3 (N = − 3). Thus reaction (*ii*) in its complete/balanced form can be obtained by adding half-reactions (*a*) and (*b*) given below :

$$(a)\ \underset{(Zn\,=\,0)}{Zn} + 4OH^- \xrightarrow{\text{Oxidation}} \underset{(Zn\,=\,+2)}{ZnO_2^{2-}} + 2H_2O + 2e^-] \times 4$$

$$(b)\ \underset{(N\,=\,+5)}{NO_3^-} + 6H_2O + 8e^- \xrightarrow{\text{Reduction}} \underset{(N\,=\,-3)}{NH_3} + 9OH^-$$

$$4Zn + NO_3^- + 7OH^- \longrightarrow 4ZnO_2^{2-} + NH_3 + 2H_2O$$

Q.7 Write the chemical equation for the reaction in which concentrated HNO_3 is mixed with conc. H_2SO_4.

Ans : According to one view the reaction between conc. HNO_3 and conc. H_2SO_4 produces nitronium ion (NO_2^+)

$$HNO_3\ (\text{conc.}) + H_2SO_4\ (\text{conc.}) \longrightarrow NO_2^+ + H_3O^+ + HSO_4^-$$

According to another view, when conc. HNO_3 is added to conc. H_2SO_4, HNO_3 gets dehydrated by H_2SO_4 and N_2O_5 is formed.

$$2HNO_3 \xrightarrow[\text{Dehydratetion }(-H_2O)]{\text{Conc. }H_2SO_4} N_2O_5 + H_2O$$

In polar solvent, N_2O_5 formed as above gives nitronium ion (NO_2^+) and nitrate ion (NO_3^-)

$$N_2O_5 \xrightarrow[\text{solvent}]{\text{In polar}} NO_2^+ + NO_3^-$$

Q.8 Write the chemical equation showing the reaction between conc. HNO_3 and conc. HCl.

Ans : When 1 part of conc. HNO_3 is mixed with 3 parts of conc. HCl, aqua regia is obtained. Aqua regia produces nescent chlorine (Cl) along with nitrosyl chloride (NOCl) or nitric oxide (NO).

$$HNO_3 + 3HCl \longrightarrow 2H_2O + NOCl + 2Cl$$
$$HNO_3 + 3HCl \longrightarrow 2H_2O + NO + 3Cl$$

Q.9 Arrange the following species in the decreasing order of ONO bond angles : NO_2, NO_2^+ and NO_2^-. Give appropriate reason for answer.

Ans : NO_2 molecule ($:\underset{\cdot\cdot}{\ddot{O}} \leftarrow \dot{N} = \ddot{O}:$). In this molecule N-atom is sp^2 hybridised but ONO bond angle is 132° which is greater that the expected value of 120° for sp^2 hybridisation. The increase in bond angle is due to the fact that $(bp - bp)$ replusions are stronger than $(lp - lp)$ repulsions.

NO_2^+ ion. ($:\ddot{O} = \overset{+}{N} = \ddot{O}:$). In this ion N^+ is sp hybridised and hence ONO bond angle = 180°.

NO_2^- ion ($:\ddot{O} = \ddot{N} - \overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:$). In this ion N-atom is sp^2 hybridised but ONO bond angle is less than (= 115°) the expected bond angle of 120° for sp^2 hybridisation. The decrease in bond angle is due to the fact that $(lp - bp)$ repulsions are stronger than $(bp - bp)$ repulsions.

Thus the decreasing order of ONO bond angles is :

$NO_2^+ (= 180°) > NO_2 (= 132°) > NO_2^- (= 115°)$

Q.10 *(i)* Write the chemical equations involved in ring test for NO_3^- ion.

***(ii)* What is oxidation state of Fe and NO in $[Fe(H_2O)_5(NO)]^{2+}$.**

Ans : *(i)* The presence of NO_3^- ion is detected by ring test. In this test a freslly prepared solution of $FeSO_4$ is added to the aqueous solution of nitrate taken in a test tube. Pure conc. H_2SO_4 is then added carefully dropwise along the walls of test tube. The appeareance of a dark brown ring at the junction of the two layers indicates the presence of NO_3^- ion. The brown ring is due to the formation of a complex ion, $[Fe\ (H_2O)_5(NO)]^{2+}$. The formation of this complex ion takes place through the following steps :

(a) NO_3^- oxidises Fe^{2+} ion (from $FeSO_4$ solution) in presence of H_2SO_4 to Fe^{3+} ion and is itself reduced to NO.

$$\underset{\text{(From FeSO}_4\text{ solution)}}{3Fe^{2+}} + NO_3^- + \underset{\text{(From H}_2\text{SO}_4)}{4H^+} \longrightarrow 3Fe^{3+} + 2H_2O + NO$$

$$[6FeSO_4 + 2KNO_3 + 4H_2SO_4 \longrightarrow 3Fe_2\ (SO_4)_3 + 4H_2O + K_2SO_4 + 2NO$$

(Molecular equation)

(b) In this step NO evolved in reaction *(a)* reacts with Fe^{2+} ions (from unreacted $FeSO_4$ solution) and forms brown coloured complex ion, $[Fe(H_2O)_5\ (NO)]^{2+}$

$$\underset{\text{(From unreacted FeSO}_4\text{ solution)}}{Fe^{2+}} + 5H_2O + NO \longrightarrow \underset{\text{Brown complex ion.}}{[Fe(H_2O)_5(NO)]^{2+}}$$

$[FeSO_4 + 5H_2O + NO \longrightarrow [Fe(H_2O)_5(NO)]\ SO_4$ *(Molecular equation)*]

(ii) O.S. of Fe and NO both is + 1 in $[Fe(H_2O)_5(NO)]^{2+}$

The formation of $[Fe(H_2O)_5(NO)]^{2+}$ as shown by chemical equation given at (*b*) above suggests that since $[Fe(H_2O)_5(NO)]^{2+}$ results from Fe^{2+} ion (O.S. = + 2) and NO (neutral molecules, O.S. = 0), O.S. of Fe and NO in $[Fe(H_2O)_5(NO)]^{2+}$ should be + 2 and zero respectively. Experiments have, however, shown that O.S. of Fe and NO both is + 1. This can be explained as follows.

Explanation. As a matter of fact, the formation of $[Fe(H_2O)_5 (NO)]^{2+}$ takes through the following steps :

(*a*) We know that NO molecule is an odd-electron molecule and hence has one unpaired electron on N-atom. This molecule loses its unpaired electron (oxidation) and is converted into nitrosonium ion, NO^+.

$$:\dot{N}=\ddot{O}: \xrightarrow{\text{Oxidation } (-e^-)} :\overset{+}{N}=\ddot{O}: + e^- \ (\textit{Nitrosonium ion})$$

(*b*) In this step the electron obtained in step (*a*) is accepted by Fe^{2+} (present in unreacted $FeSO_4$) which is reduced to Fe^+ ion.

$$Fe^{2+} \text{ (From } FeSO_4) + e^- \xrightarrow{\text{Reduction } (+e^-)} Fe^+$$

(*c*) Fe^+ ion formed in step (*b*) combines with NO^+ ion formed in step (*a*) and gives brown complex ion, $[Fe^+(H_2O)_5 (NO^+)]^{2+}$,

$$Fe^+ + NO^+ + 5H_2O \longrightarrow \underset{\text{Brown complex ion}}{[Fe^+(H_2O)_5 (NO^+)]^{2+}}$$

Above discussion shows that the brown ring complex ion, $[Fe(H_2O)_5(NO)]^{2+}$ is formed due to charge-transfer, since an electron is transfered from NO to Fe^{2+}. In $[Fe(H_2O)_5(NO)]^{2+}$ ion, since Fe and NO both are in + 1 oxidation state, this complex ion is called *pentaquanitrosonium iron (I) ion*.

Alternative explanation based on magnetic moment value. The presence of Fe and NO as Fe^+ and NO^+(NO^+ ion is a two-electron donor ligandions in $[Fe(H_2O)_5(NO)]^{2+}$ ion is also confirmed by the magnetic property of $[Fe(H_2O)_5 (NO)]^{2+}$ ion. It has been found that the complex ion is paramenetic and its magnetic moment value is equal to 3.9 B.M.[$\mu = \sqrt{n(n+2)}$) B.M. = $\sqrt{3\,(3+2)}$ B.M. = 3.87 BM] (n = 3)]. Now the valence-shell configurations of Fe^+, Fe^{2+} and Fe^{3+} ions (= 1, + 2 and + 3 are common oxidation states of Fe) as given below show that it is only Fe^+ ion which has three unpaired electrons.

Fe $(3d^6 4s^2) = 3d^2\ 3d^1\ 3d^1\ 3d^1\ 3d^1\ 4s^2\ (n = 4)$

Fe^+ $(3d^6\ 4s^1) = 3d^7\ 4s^{\circ} = 3d^2\ 3d^2\ 3d^1\ 3d^1\ 3d^1\ 4s^{\circ}\ (n = 3)$

Fe^{2+} $(3d^6 4s^0)\ 3d^2\ 3d^1 = 3d^1\ 3d^1\ 3d^1\ 4s^0\ (n = 4)$

Fe^{3+} $(3d^5\ 4s^0) = 3d^1\ 3d^1\ 3d^1\ 3d^1\ 3d^1\ 4s^{\circ}\ (n = 5)$

$[Fe(H_2O)_5(NO)]^{2+}$ ion is an octahedral complex ion, since C.N. of Fe^+ ion (central metal ion) is 6. Since H_2O and NO^+ are weak ligands, $[Fe(H_2O)_5(NO)]^{2+}$ ion results from sp^3d^2 hybridisation of Fe^+ ion. This hybridisation gives n = 3. Due to sp^3d^2 hybridisation $[Fe(H_2O)_5(NO)]^{2+}$ ion is a HS octahedral complex ion.

Q.11 When conc. H_2SO_4 was added into an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified when copper turnings were also added into this test tube. On cooling, the gas

(A) changed into a colourless gas (B). Identity the gases (A) and (B). Write the equations for the reactions involved.

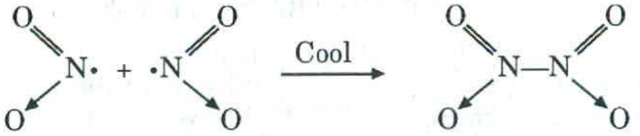
Ans : When a nitrate salt is heated with conc. H_2SO_4, vapours of HNO_3 are first produced which undergo decomposition to produce nitrogen dioxide (NO_2) which is a brown gas (A). When Cu turnings are added, the gas (A) intersified due to the reduction of HNO_3 by Cu.

$$\underset{\text{Sod. nitrate}}{2NaNO_3} + H_2SO_4 \xrightarrow{\text{Heat}} \underset{\substack{\text{Nitric acid}\\ (\textit{Colourless})}}{2HNO_3} + Na_2SO_4$$

$$4HNO_3 \xrightarrow{\text{Heat}} \underset{\substack{\text{Nitrogen dioxide}\\ (\textit{Brown gas A})}}{4NO_2} + O_2 + 2H_2O$$

$$\underset{\text{Copper turnings}}{Cu} + 4HNO_3 \xrightarrow{\text{Heat}} Cu(NO_3)_2 + \underset{\substack{\text{Nitrogen}\\ \text{dioxide (A)}}}{2NO_2} + 2H_2O$$

Since NO_2 gas formed in the above reaction is an odd electron molecule ($e = 7 + 2 \times 8 = 23$), this molecule, on cooling, dimeries to form a colourless gas, N_2O_4. N_2O_4 is more stable than NO_2.



Nitrogen dioxide (NO_2) (*Brown gas, A*) Dinitrogen tetroxide (N_2O_4) (*Colourless gas, B*)

Thus, (A) is nitrogen dioxide (NO_2) and (B) is dinitrogen tetroxide (N_2O_4).

University Questions

1. Write a note on "Hydrides of nitrogen". *(Utkal 86)*

2. Explain why a mixture of hydrazine and H_2O_2 in presence of Cu (II) catalyst is used as a rocket propellant. *(I.I.T. 87)*

3. Draw the resonating structures of N_3^- ion. *(Punjab 83)*

4. Write a detailed note on "Hydroxylamine". *(Delhi 88)*

5. Discuss the structure of various oxides of nitrogen. *(G.N.D. 82)*

6. Draw the electron dot structures of the oxy acids of nitrogen. *(Meerut 85)*

7. Write a note on "Pernitric acid". *(Madras 86)*

8. Write short note on "Hydrazoic acid". *(Delhi 99)*

9. Describe the action of heat on hydrazine. Give balanced chemical equation. *(Delhi 99)*

10. Discuss the structure and constitution of hyponitrous acid. *(Allahabad 99)*

(*a*) How does hydrazine react with (*i*) $AgNO_3$ (*ii*) HONO.

(*b*) Give two methods to prepare hydroxylamine.*(Himachal Pradesh 2000)*.

11. (*i*) Describe the method of preparation, structure and uses of hydrazoic acid or hyponitrous acid.

(*ii*) Explain why PH_3 is more volatile than NH_3 ?[*Gauhati (General) 2000*]

CHAPTER

33

Nitrides

What are Nitrides ?

The binary compounds of nitrogen with electropositive elements or with the elements which are less electronegative than nitrogen are called nitrides.

This definition does not include the salts of hydrazoic acid, HN_3 (*e.g.* NaN_3). Rather the salts of hydrazoic acid are called *azides*. Thus, NaN_3, AgN_3 etc. are the examples of azides while Na_3N, Ag_3N etc. are the examples of nitrides.

General Methods of Preparation

1. By direct combination of elements. Combination is brought about generally by heating the element in a current of nitrogen to a suitable temperature.

In the case of alkaline earth metals, amalgam may be used in place of the pure metal.

$$6Li + N_2 \longrightarrow 2Li_3N$$
$$3Mg + N_2 \longrightarrow Mg_3N_2$$
$$2Al + N_2 \longrightarrow 2AlN$$

In some cases, as for instance aluminium and chromium, the combination is effected by striking an electric arc between metal electrodes in an atmosphere of nitrogen. In the case of alkali metals, *active nitrogen* is used in place of ordinary nitrogen.

2. By heating the element, its oxide or chloride with NH_3. The elements or their oxides are heated with NH_3 at 300–400°C to get their nitrides. The nitrides of Mg, Zn, Ag, B, Al, Fe, Co, Ni etc. can be obtained by this method.

$$3Mg + 2NH_3 \longrightarrow Mg_3N_2 + 3H_2$$
$$6Cu + 2NH_3 \longrightarrow 2Cu_3N + 3H_2$$
$$3Fe + 2NH_3 \longrightarrow Fe_3N_2 + 3H_2$$
$$3ZnO + 2NH_3 \longrightarrow Zn_3N_2 + 3H_2O$$
$$3Ag_2O + 2NH_3 \longrightarrow Ag_3N + 3H_2O$$
$$3CuO + 2NH_3 \longrightarrow Cu_3N_2 + 3H_2O$$
$$B_2O_3 + 2NH_3 \longrightarrow 2BN + 3H_2O$$

The nitrides of the elements like Ti, Zr, Th, Cr, Mo, W, U, B etc. have been prepared by passing their chloride vapour with NH_3 through a tube heated to 800°C.

$$BCl_3 + NH_3 \xrightarrow{800°C} BN + 3HCl$$

3. By the action of nitrogen on a mixture of metallic oxide and carbon. The reaction is carried out at a high temperature in an electric furnace. At the high temperature carbon reduces the oxide to the metal which reacts with nitrogen to form the nitride. Nitrides of aluminium, zirconium, scandium, niobium and boron are prepared in this way.

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO \uparrow$$
$$B_2O_3 + 3C + N_2 \longrightarrow 2BN + 3CO \uparrow$$
$$ZrO + C + N_2 \longrightarrow ZrN_2 + 3CO \uparrow$$

4. By heating amides and imides . Amides and imides, on heating, decompose to give the nitrides. For example :

$$3Ba(NH_2)_2 \xrightarrow{\Delta} 4Ba_3N_2 + NH_3 \uparrow$$
$$3Ca(NH_2)_2 \xrightarrow{\Delta} Ca_3N_2 + 4NH_3 \uparrow$$
$$3Zn(NH_2)_2 \xrightarrow{\Delta} Zn_3N_2 + 4NH_3 \uparrow$$
$$B_2(NH)_3 \xrightarrow{\Delta} 2BN + NH_3 \uparrow$$
$$As_2(NH)_3 \xrightarrow{\Delta} 2AsN + NH_3 \uparrow$$

5. By heating the element with NO. Under suitable conditions, certain elements combine with NO to form nitrides.

$$5B + 3NO \longrightarrow 3BN + B_2O_3$$

6. By the action of N_2 on hydrides. The nitrides of certain metals can be prepared by heating their hydrides in a current of N_2.

$$3MgH_2 + 2N_2 \longrightarrow Mg_3N_2 + 2NH_3 \uparrow$$
$$3BaH_2 + 2N_2 \longrightarrow Ba_3N_2 + 2NH_3 \uparrow$$

7. By the action of a halide on amide. When halides and amides of certain metals are mixed together, nitride of the metal (whose halide has been taken) is formed.

$$BiCl_3 + 3KNH_2 \longrightarrow BiN + 3KCl + 2NH_3$$

8. By the action of cyanides on nitrates. Some nitrides have been obtained by the action of cyanides on nitrates.

$$3Cu(CN)_2 + 12NH_4NO_3 \longrightarrow Cu_3N_2 + 24H_2O + 6CO_2 + 14N_2$$

General Properties

1. Action of water. Nitrides react with water to produce ammonia gas. The rate of hydrolysis varies with the nature of the nitride and some of them (*e.g.*, alkaline earth metals, Mg and Zn nitrides) are decomposed even by the moisture present in air and the reaction is quite vigorous with water. Where as Mn_4N_3 and W_2N_3 are only slowly hydrolysed by water, CrN is not decomposed even by steam at 220°C.

$$Li_3N + 3H_2O \longrightarrow 3LiOH + 2NH_3$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

$$BN + 3H_2O \longrightarrow B(OH)_3 \text{ or } H_3BO_3 + NH_3$$

2. Action of hydrogen. Nitrides are reduced by hydrogen with the formation of hydrides and evolution of ammonia.

$$Mg_3N_2 + 6H_2 \longrightarrow 3MgH_2 + 2NH_3$$

$$CeN + 3H_2 \longrightarrow CeH_3 + NH_3$$

3. Action of acids. Nitrides are decomposed by dilute acids producing the salt of the metal atom present in the nitride.

$$2Cu_3N + 8HCl \longrightarrow 2NH_4Cl + 6CuCl$$

$$2CeN + 4H_2SO_4 \longrightarrow Ce_2(SO_4)_3 + (NH_4)_2SO_4$$

4. Action of alkalies. Caustic alkalies decompose nitrides liberating ammonia gas.

$$AlN + 3KOH \longrightarrow K_3AlO_3 + NH_3 \uparrow$$

$$BN + 3KOH \longrightarrow K_3BO_3 + NH_3 \uparrow$$

5. Action of halogens. Nitrides react with halogens at 700°C giving N_2 gas.

$$2AlN + 3Cl_2 \longrightarrow 2AlCl_3 + N_2 \uparrow$$

6. Action of CO and CO_2. CO and CO_2 decompose nitrides at about 200°C to form metal oxides. For example :

$$Mg_3N_2 + 3CO \longrightarrow 3MgO + 3C + N_2$$

$$Mg_3N_2 + 3CO_2 \longrightarrow 3NgO + 3CO + N_2$$

7. Sublimation. There are many nitrides which, like oxides, sublime. For example gallium nitride sublimes without decomposition above 800°C.

Classification of Nitrides

The nitrides have been classified into three types depending on the nature of bonding between nitrogen and the other element. These three types are: (1) *Ionic or salt-like nitrides* (2) *Covalent nitrides*, (3) *Interstitial or metallic or alloy nitrides*.

Ionic Nitrides

These are ionic in nature and contain the nitride ion, N^{3-}. These are given by the elements of groups IA (alkali metals), IIA (alkaline earth metals), Zn, Cd, Cu(*ous*), Ag.

Preparation.

Ionic nitrides are prepared : (*i*) by direct union of the elements.

$$6Li + N_2 \longrightarrow 2Li_3N$$

$$3Mg + N_2 \longrightarrow Mg_3N$$

(*ii*) by passing NH_3 over heated metal or its oxide.

$$3Mg + 2NH_3 \longrightarrow Mg_3N_2 + 3H_2 \uparrow$$

$$3Ag_2O + 2NH_3 \longrightarrow 2Ag_3N + 3H_2O$$

(*iii*) by decomposing the amide at elevated temperature

$$3Ba(NH_2)_2 \xrightarrow{\Delta} Ba_3N_2 + 4NH_3$$

Properties.

These are crystalline colourless compounds having high melting points. These are hydrolysed by H_2O to form the hydroxides and NH_3.

$$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$$

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$$

When heated in a current of CO_2 at 200°C, N_2 gas is evolved.

$$Mg_3N + 3CO_2 \longrightarrow 3MgO + 3CO + N_2$$

When heated in a current of H_2S, sulphides are obtained.

$$Mg_3N_2 + H_2S \longrightarrow 3MgS + (NH_4)_2S$$

Structure.

Ionic nitrides contain metal ions in combination with nitride ion, N^{3-}. The structure of Li_3N is written as $Li^+[Li^+ - N^{3-} - Li^+]^-$. This nitride has a hexagonal structure.

The nitrides of M_3N_2 type are *anti-isomorphous* with oxides of M_2O_3 type, metal atoms occupying oxygen positions and N-atoms occupying metal positions in the oxide structure.

Covalent Nitrides

These nitrides are formed by the sharing of electrons between nitrogen and the metal or non-metal. This type of nitrides some volatile nitrides of non-metals such as H, C, Si. P, Cl, F etc. and some non-volatile nitrides, of the elements of group IIIA like B, Al, Ga and In. Thus the compounds like NH_3, cyanogen and oxides and halides of nitrogen are the examples of volatile covalent nitrides while BN, AlN, Si_3N_4, P_3N_5 are non-volatile covalent nitrides. The non-volatile nature of the nitrides is attributed to their macro-molecular structures. For example BN has a layer-like structure which is analogous to that of graphite and crystal structure of AlN is very similar to that of diamond. Non-volatile covalent nitrides undergo hydrolysis to give NH_3.

$$BN + 3H_2O \longrightarrow B(OH)_3 \text{ or } H_3BO_3 + NH_3$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

Interstitial Nitrides

These nitrides are given by transition metals. On heating, transition metals of groups IIIB. IVB and VB absorb N_2 to give the nitrides of MN type. Mo_2N, W_2N, Fe_4N and Mn_4N nitrides are also known. In these nitrides N-atoms occupy the holes in the metallic lattice. The atomic radius of transition metals is sufficiently greater to allow the inclusion of N-atoms in the holes in the metallic lattice.

Preparation.

These nitrides are obtained (*i*) by heating powdered metal in N_2 or NH_2 at 1100–1300°C (*ii*) by heating metal filaments in N_2 (*iii*) by heating a carrier filament (*e.g.* Pt, W or C) in a mixture of N_2 and metal halide vapours and subsequently removing the carrier by high temperature volatilisation.

Properties.

Being nitrogen deficient, these nitrides are often not exactly stoichiometric. They have some metallic properties, *e.g.* they are extremely hard and electrical conductors, since electrical structure of metal persists in these nitrides. They are stable and very inert. They do not hydrolyse. These have very high melting points. For example UN has its melting point equal to 2570°C. Some nitrides are isomorphous to oxides and carbides. For example TiN is isomorphous to TiO and TiC.

Structure.

The structure of nitrides is usually cubic like rock-salt. Nitrogen atoms in the nitrides of MN type occupy all the octahedral holes while in Mc_2N and W_2N nitrides only one-half of the octahedral holes are occupied by N-atoms and in Mn_4N and Fe_4N nitrides only one-quarter of octahedral holes are occupied by N-atoms. Thus we see that the nitrides of MN type have NaCl type structure.

Uses of Nitrides

1. BN possesses same hardness as diamond and can withstand temperature of more than 300°C. Due to this property it is used for coating crucible lining.

2. The formation of AlN during the purification of bauxite by Serpeck's process is utilised for the manufacture of NH_3.

Questions with Answers

Q.1 Element A burns in N_2 to give an ionic compound, B. Compound B reacts with H_2O to give C and D. A soution of C becomes milky on bubbling CO_2. Identity A, B, C and D. ***(I.I.T. 1997)***

Ans : A = Ca, B = Ca_3N_2, C = $Ca(OH)_2$ and D = NH_3

Explanation (*i*) Since A burns in N_2 to give an ionic compound B, B must be the nitride of a metal, *i.e.* A must be a metal.

$$\text{A (Metal)} + N_2 \longrightarrow \underset{\text{(B)}}{\text{Metallic nitride of A}}$$

(*ii*) Since compound B is a metallic nitride, it should give hydroxide of A and NH_3 with H_2O. Thus D is NH_3

$$B + H_2O \longrightarrow \underset{\text{(C)}}{\text{Hydroxide of A}} + \underset{\text{(D)}}{NH_3}$$

(*iii*) Since solution of C (*i.e.* hydroxide of A) becomes milky on bubbling CO_2, milkiness is due to the formation of $CaCO_3$. Thus A metal is Ca and C must be $Ca(OH)_2$. Obviously B is Ca_3N_2.

Reactions can now be shown as :

$$\underset{(A)}{2Ca} + N_2 \xrightarrow{\Delta} \underset{(B)}{Ca_3N_2} \text{ (Ionic compound)}$$

$$\underset{(B)}{Ca_3N_2} + 6H_2O \longrightarrow \underset{(C)}{Ca(OH)_2} + \underset{(D)}{2NH_3}$$

$$\underset{(C)}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\substack{(D)\\(Milkiness)}}{CaCO_3} + H_2O$$

Q.2 Calcium burns in nitrogen to produce a white powder which dissolves in suffecient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer (B) on the surface. Identity the compounds (A) and (B). ***(I.I.T. 1996)***

Ans : A = NH_3, B = $CaCO_3$

Explanation : Ca burns in N_2 to give white powder of Ca_3N_2

$$3Ca + N_2 \xrightarrow{\Delta} Ca_3N_2 \text{ (White powder)}$$

This white powder of Ca_3N_2 dissolves in H_2O to produce NH_3 (which is a gas) and alkaline solution of $Ca(OH)_2$. Thus A is NH_3.

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + \underset{(A)}{2NH_3} \text{ (Gas)}$$

Alkaline solution of $Ca(OH)_2$ reacts with CO_2 present in the atmosphere (air) and produces $CaCO_3$ which gets deposited as a layer on the surface. Thus B is $CaCO_3$.

$$Ca(OH)_2 + CO_2 \text{ (From air)} \longrightarrow \underset{(B)}{CaCO_3} + H_2O$$

University Questions

1. How are nitrides classified ? Give a brief account of interstitial nitrides. *(Madras 86; Bharathiar 86)*
2. Describe the preparation, properties, uses and structure of boron nitride. *(Bharathiar 86; Jodhpur 85; Agra 80, 82, 84)*
3. How does BN resemble with and differ from graphite ? *(Bharathiar 86)*
4. Give the preparation, properties and uses of magnesium nitride. *(Gorakhpur 85)*
5. Write balanced equation for :
   $Mg_3 N_2 + H_2O \longrightarrow . . . .$ *(Bharathiar 86)*
6. Describe the action of heat of Li_3N. *(Delhi 99)*
7. Write the action of H_2O, H_2, acids, alkalies, halogens, CO and CO_2 on nitrides.

CHAPTER

34

Oxides, Oxy acids, Halides and Oxy halides of Phosphorus

Oxides

1. Phosphorus Trioxide, P_2O_3 or P_4O_6.

Preparation. This oxide is also called *phosphorus sesquioxide* and is the *anhydride of phosphorus acid*, H_3PO_3. It is prepared when white phosphorus is treated with a restricted supply of O_2. It is better prepared in the low pressure reaction of phosphorus vapour with N_2O at 600°C.

$$P_4 \text{ (vapour)} + 6N_2O \xrightarrow{600°C} 2P_2O_3 + 6N_2$$

Properties. It is a snow white wax-like solid and has garlic smell. When impure it is waxy. It is poisonous. P_2O_3 melts at 23.6° and boils at 17.4°C.

When heated to about 440°C, it dissociates to give phosphorus dioxide and red phosphorus.

$$2P_2O_3 \longrightarrow 3PO_2 + P$$

When P_2O_3 is shaken with ice water, it gives phosphorous acid. (H_3PO_3). Hence this oxide is also called anhydride of H_3PO_3

$$P_2O_3 + 2H_2O \longrightarrow 2H_3PO_3$$

With hot water, the reaction is violent and phosphoric acid with some phosphine is produced.

$$2P_2O_3 + 6H_2O \longrightarrow 3H_3PO_4 + PH_3$$

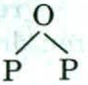
P_2O_3 oxidises in air or O_2 to peroxide (P_2O_6), inflames at 70°C in air and at 40°C in O_2

$$2P_2O_3 + 3O_2 \longrightarrow 2P_2O_6$$

It inflames spontaneously in Cl_2 and forms phosphoryl chloride, $POCl_3$ and perhaps meta phosphoryl chloride, PO_2Cl.

It combines violently with sulphur forming crystalline $P_4O_6S_4$.

Structure. The vapour density of the oxide and the lowering of the freezing point of its solution in benzene correspond to the formula P_4O_6. Thus phosphorus trioxide exists as the dimer, P_4O_6. The structure of P_4O_6 molecule in the vapour state can be derived from that of P_4 molecule which has tetrahedral structure. If in the tetrahedral structure of P_4 molecule six oxygen atoms are placed just outside the mid points of the six edges of the tetrahedron to form six



bridges, we get the structure of P_4O_6 molecule. Thus in the structure of P_4O_6 molecule each P-atom is covalently bonded to three O-atoms and each O-atom is covalently bonded to two P-atoms. In this way all the four P-atoms and six O-atoms have eight electrons in their valence shells and we have *six non-linear* P—O—P arrangements. Here it may be noted that P—P bonds are absent in this molecule, although in the structure of P_4 molecule there are six P—P bonds. The P—O bond length is 1.65A° which is about the P—O single bond distance and the bond angles POP and OPO are 127.6 and 99° respectively. Since each P-atom is tricovalent in this molecule, an unused electron pair (called lone pair) is left on each P-atom (Fig. 34.1).

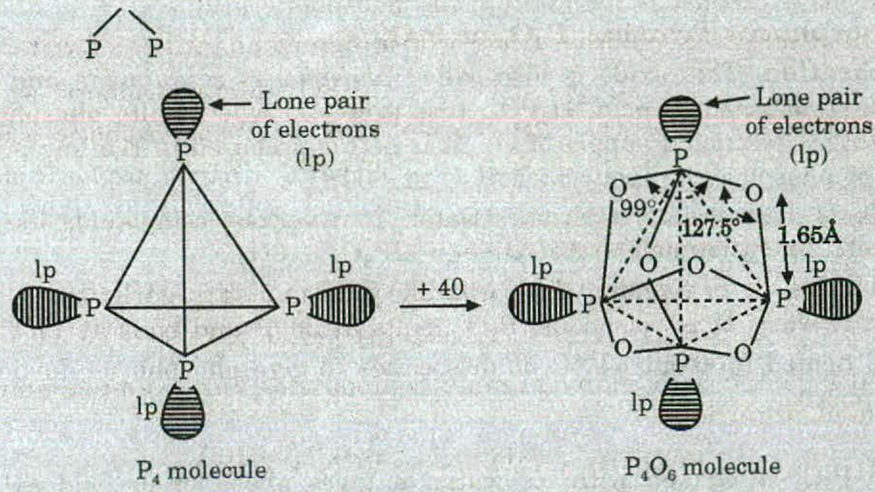


Fig. 34.1. Structure of P_4 ant P_4O_6 molecules.

2. Phosphorus Tetroxide, P_2O_4.

This oxide was discovered by Thrope and Tutton in 1886. It is prepared by heating P_2O_3 in a sealed tube at 440°C or by heating a mixture of P_2O_3 and P_2O_5 in a sealed tube to 290°C.

(*a*) $4P_2O_3 \longrightarrow 3P_2O_4 + 2P$

(*b*) $P_2O_3 + P_2O_5 \longrightarrow 2P_2O_4$

In reaction (*a*) P_2O_4 appears as a crystalline sublimate while red phosphorus remains as a residue. It is a colourless crystalline solid. The vapour density at 1800°C corresponds with the formula P_5O_{16}. With H_2O it gives a mixture of H_3PO_3 and H_3PO_4.

$$P_2O_4 + 3H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

Thus P_2O_4, like N_2O_4, may be regarded as a *mixed anhydride* of phosphorus acid (H_3PO_3) and phosphoric acid (H_3PO_4).

3. Phosphorus Pentoxide, P_2O_5 or P_4O_{10}.

Preparation. It is obtained when white phosphorus burns in excess of air in iron drums or when white phosphorus is burnt in CO_2 at 100°C.

$$4P + 5O_2 \longrightarrow 2P_2O_5$$
$$2P + 5CO_2 \longrightarrow P_2O_5 + 5CO$$

It can be purified by sublimation in oxygen at about 360°C.

Properties. Phosphorus pentoxide is a white powdery solid, having a garlic smell which is due to presence of traces of the trioxide. Pure pentoxide has no smell. Its vapour density corresponds to the formula P_4O_{10} but it is generally represented by the formula P_2O_5. It exhibits a strong phosphorescence after illumination especially at low temperatures.

It gives phosphoric acid with water.

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

The main product is definitely ortho phosphoric acid.

It, however, gives different acids with different quantities of water *e.g.*,

$$P_2O_5 + H_2O \longrightarrow 2HPO_3 \text{ (Metaphosphoric acid)}$$
$$P_2O_5 + 2H_2O \longrightarrow H_4P_2O_7 \text{ (Pyrophosphoric acid)}$$
$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \text{ (Orthophosphoric acid)}$$

P_2O_5 is hygroscopic. It absorbs water from various compounds like H_2SO_4, HNO_3 etc. and thus dehydrates them

$$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$$
$$2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$$

It also dehydrates many organic compounds. For example amides are dehydrated to nitrides.

$$RCONH_2 + P_2O_5 \longrightarrow RCN + 2HPO_3$$

For the same reason, P_2O_5 chars wood, paper, sugar etc.

It gives meta phosphates with alkalies

$$P_2O_5 + 2NaOH \longrightarrow \underset{\text{sodium meta phosphate}}{2NaPO_3} + H_2O$$

It is reduced to red phosphorus when heated with carbon.

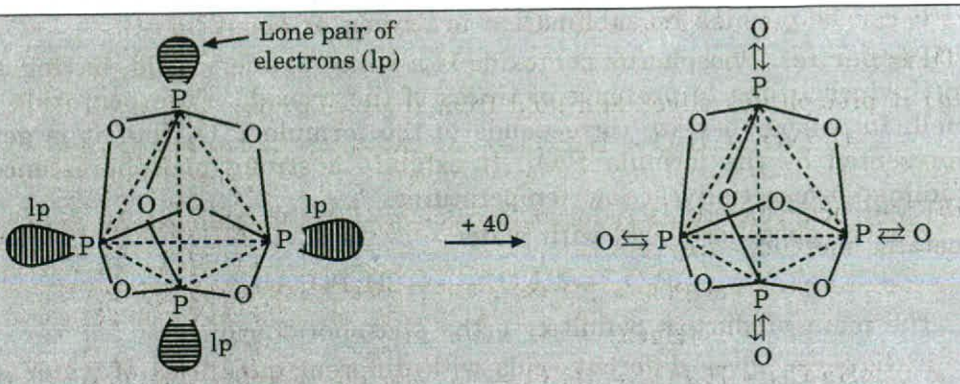
$$P_2O_5 + 5C \longrightarrow \underset{\text{Red phosphorus}}{2P} + 5CO$$

When fused with basic oxides it gives solid phosphates.

$$6CaO + 2P_2O_5 \longrightarrow 2Ca_3(PO_4)_2$$

It is extensively used as a *drying* and a *dehydrating* agent in the laboratory.

Structure. The vapour density of this oxide corresponds to the formula P_4O_{10}. The structure of this molecule can be derived from that of P_4O_6 molecule. If four additional oxygen atoms are bonded to four phosphorus atoms by a P→O co-ordinate bond, we get the structure of P_4O_{10} (Fig. 34.2). P→O co-ordinate bond is formed by the donation of a lone pair on phosphorus atom. The length of this P—O bond is 1.39A° which is much shorter than the length of other P—O bonds (= 1.65A°) in the molecule. This much shorter value is explained by $p\pi(O)$—$d\pi(P)$ *back bonding via* lateral overlap of a filled *p*-orbital of oxygen atom with a vacant *d*-orbital of phosphorus atom.



P_4O_6 molecule

P_4O_{10} molecule

Fig. 34.2. Structure of P_4O_{10} molecule.

4. Phosphorus Peroxide, PO_3 or P_2O_6.

It is formed when an electric discharge is passed through a mixture of P_2O_5 vapour and oxygen at about 1 mm. pressure. It is a violet solid which when heated to 130°C gives P_2O_5 and O_2. Its aqueous solution liberates iodine from K solution.

Oxy-acids

1. Hypophosphorus Acid, H_3PO_2.

Preparation. This acid is manufactured from borium hypophosphite, $Ba(H_2PO_2)_2$. When phosphorus is boiled with baryta solution (barium hydroxide solution), $Ba(H_2PO_2)_2$ is formed, which is filtered out.

$$3Ba(OH)_2 + 8P + 6H_2O \longrightarrow \underset{\text{ppt.}}{3Ba(H_2PO_2)_2} + 2PH_3$$

If to this barium salt, sulphuric acid be added in calculated amounts, and the solution filtered, free hypophosphorus acid comes down ‘in the filtrate.

$$Ba(H_2PO_2)_2 + H_2SO_4 \longrightarrow \underset{\text{ppt.}}{BaSO_4} + 2H_3PO_2$$

The filtrate, when evaporated leaves the syrupy acid, and when carefully cooled below 0°, can be crystallised out also.

Properties. (*i*) It is a colourless crystalline solid having specific gravity 1.492 and m.pt = 26.5°. It is readily soluble in water.

(*ii*) *Action of heat.* When strongly heated, the acid is decomposed to phosphine.

$$2H_3PO_2 \longrightarrow PH_3 + H_3PO_4$$

The salts of the acid also decompose on heating and evolve PH_3.

(*iii*) *Action of nascent hydrogen.* H_3PO_2 is reduced to PH_3 by nascent hydrogen (Zn + dil. H_2SO_4).

$$H_3PO_2 + 4H \longrightarrow PH_3 + 2H_2O$$

(*iv*) *Reducing properties.* The acid and its salts are powerful reducing agents. The potential equation for these reductions is :

$$H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$$

Thus :

(*a*) It precipitates silver and gold from their solutions.

$$4AgNO_3 + H_2O + H_3PO_2 \longrightarrow \underset{\text{ppt.}}{4Ag} + 4HNO_3 + H_3PO_3$$

(*b*) Mercuric chloride is reduced to calomel (mercurous chloride) and finally to metallic mercury (grey ppt.)

$$H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$$

$$4HgCl_2 + 4H \longrightarrow 2Hg_2Cl_2 + 4HCl$$

$$4Hg_2Cl_2 + H_3PO_2 + 2H_2O \longrightarrow \underset{\text{Calomel}}{2Hg_2Cl_2} + 4HCl + H_3PO_4$$

$$2Hg_2Cl_2 + H_3PO_2 + 2H_2O \longrightarrow \underset{\substack{\text{Metallic mercury}\\ \text{(grey ppt.)}}}{4Hg} + H_3PO_4 + 4HCl$$

(*c*) I_2 reduces Cl_2 and I_2 to HCl and HI respectively.

$$H_3PO_2 + 2H_2O \longrightarrow H_3PO_3 + 4H$$

$$2X_2 + 4H \longrightarrow 4HX$$

$$\underset{(X = Cl,\ I)}{2X_2} + H_3PO_2 + 2H_2O \longrightarrow 4HX + H_3PO_4$$

(*d*) Copper salts on warming with the acid give a brown precipitate of cuprous hydride, CuH

$$4CuSO_4 + 3H_3PO_2 + 6H_2O \longrightarrow 4CuH + 3H_3PO_4 + 4H_2SO_4$$

(*v*) *Action of active metals.* Active metals like Zn, Mg etc. dissolve in the acid and H_2 is evolved.

$$Zn + 2H_3PO_2 \longrightarrow Zn(H_2PO_2)_2 + H_2$$

(*vi*) *Acidic nature.* It is a strong *monobasic* acid and ionises as follows :

$H_3PO_2 \rightleftarrows H^+ + \underset{\substack{\text{Hypophos-}\\ \text{phite ion}}}{[H_2PO_2^-]}$; Ionisation constant $= 1 \times 10^{-2}$

Hypophosphites. The salts of the acid are called *hypophosphites.* These salts are mostly soluble in water. They possess reducing properties as the acid itself has.

Uses. Some of its salts *e.g.*, those of sodium, potassium and calcium are used in medicine as nerve tonics.

2. Orthophosphorus Acid or Phosphorus Acid, H_3PO_3.

Preparation. It is prepared : (*i*) by adding phosphorus trichloride to cold water. Since the reaction is very violent, the addition should be done slowly. (*ii*) by adding PCl_3 to anhydrous oxalic acid. In this case the reaction is not violent and by-products are gases.

$$PCl_3 + 3H.OH \longrightarrow H_3PO_3 + 3HCl$$

$$PCl_3 + 3(COOH)_2 \longrightarrow H_3PO_3 + 3CO + 3CO_2 + 3HCl$$

The solution in both cases is concentrated to get orthophosphorus acid as white crystals.

Properties. (*i*) It forms white deliquescent crystals (m.pt. = 73.6°C) and is extremely soluble in water.

(*ii*) *Acidic nature.* It is a *dibasic acid* and ionizes as :

$$H_3PO_3 \rightleftarrows H^+ + H_2PO_3^- \; ; \; K_1 = 1 \times 10^{-2}$$
$$H_2PO_3^- \rightleftarrows H^+ + HPO_3^{2-} \; ; \; K_2 = 2 \times 10^{-7}$$

From the mode of its ionisation shown above it is evident that the acid gives two types of salts *viz. primary phosphite*, (*e.g.* MH_2PO_3) and *secondary phosphites* (*e.g.* M_2HPO_3).

(*iii*) *Decomposition.* When heated it gives ortho phosphoric acid and phosphine.

$$4H_3PO_3 \xrightarrow{200°} 3H_3PO_4 + PH_3$$

(*iv*) *Reducing properties.* Ortho phosphorus acid is a strong reducing agent. The potential equation is :

$$H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2H$$

Thus : (*a*) *It reduces mercuric chloride to mercurous chloride,*

$$2HgCl_2 + H_3PO_3 + H_2O \longrightarrow HgCl_2 + 2HCl + H_3PO_4$$

(*b*) *Copper sulphate is reduced to metallic copper.*

$$CuSO_4 + H_3PO_3 + H_2O \longrightarrow H_3PO_4 + Cu + H_2SO_4$$

(*c*) *Silver nitrate is reduced to metallic silver*

$$2AgNO_2 + H_3PO_3 + H_2 \longrightarrow 2Ag + 2HNO_3 + H_3PO_4$$

(*d*) *It decolorises acidified potassium permanganate solution.*

$$2KMnO_4 + 3H_2SO_4 + 5H_3PO_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 5H_3PO_4 + 3H_2O$$

(*e*) *It reduces iodine to hydriodic acid*

$$I_2 + H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 3HI$$

(*f*) *Sulphur dioxide is reduced to sulphur.*

$$2H_3PO_3 + SO_2 \longrightarrow 2H_3PO_4 + S$$

(*v*) *Action of nascent hydrogen.* It is reduced to PH_3 by ascent hydrogen (Zn + dil. H_2SO_4)

$$H_3PO_3 + 6H \longrightarrow PH_3 + 3H_2O$$

(*vi*) *Action of PCl_5.* It reacts with PCl_5 and forms PCl_3 and $POCl_3$.

$$H_3PO_3 + 3PCl_5 \longrightarrow PCl_3 + 2POCl_3 + 3HCl$$

3. Hypophosphoric Acid, $H_4P_2O_6$.

Preparation. When phosphorus is exposed to a limited supply of moist air, the acid, along with phosphorus and phosphoric acid, is produced. The resulting solution is partly neutralised with Na_2CO_3 when sparingly soluble sodium salt, $Na_2H_2P_2O_6 . 6H_2O$ separates slowly. Now $Pb(NO_3)_2$ solution is added to the solution of the salt when lead hypophosphate, $Pb_2P_2O_6$ is precipitated. The precipitate of $Pb_2P_2O_6$ is suspended in water and a current of H_2S a passed through the solution when PbS is precipitated and a solution of free $H_4P_2O_6$ is obtained. The precipitated PbS is filtered off and the filtrate is evaporated in a vacuum desiccator over H_2SO_4 when rhombic crystals of the dihydrate. $H_4P_2O_6 . 2H_2O$ separate. On further desiccation of the crystals over H_2SO_4 in vacuum, anhydrous $H_4P_2O_6$ acid is produced.

Properties. (*i*) The dihydrated acid, $H_4P_2O_6.2H_2O$ forms rhombic crystals which melt at 62°C. The anhydrous acid melts at 70°C.

(*ii*) *Acidic nature.* It is a tetrabasic acid and ionises as follows :

$$\begin{aligned} H_4P_2O_6 &\rightleftarrows H^+ + H_3P_2O_6^- \ ; K_1 = 6.4 \times 10^{-3} \\ H_3P_2O_6^- &\rightleftarrows H^+ + H_2P_2O_6^{2-} \ ; K_2 = 1.5 \times 10^{-3} \\ H_2P_2O_6^{2-} &\rightleftarrows H^+ + HP_2O_6^{3-} \ ; K_3 = 5.4 \times 10^{-8} \\ HP_2O_6^{3-} &\rightleftarrows H^+ + P_2O_6^{4-} \ ; K_4 = 9.4 \times 10^{-11} \end{aligned}$$

Its salts like $Na_2H_2P_2O_6$, $Pb_2P_2O_6$ etc. and the ester $(C_2H_5)_2P_2O_6$ have been prepared.

(*iii*) *Action of heat.* When heated above its melting point, it decomposes into H_3PO_3 and HPO_3

$$H_4P_2O_6 \longrightarrow H_3PO_3 + HPO_3$$

On heating at 180°, PH_3 is evolved

$$4H_4P_2O_6 \longrightarrow 3H_3PO_4 + 4HPO_3 + PH_3$$

(*iv*) *Hydrolysis.* The aqueous solution of the acid undergoes hydrolysis on being heated with mineral acid

$$H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

(*v*) The acid has no reducing properties.

4. Orthophosphoric Acid or Phosphoric Acid, H_3PO_4.

Manufacture. H_3PO_4 is manufactured from bone ash. The process consists of the following steps :

(*a*) When bone ash obtained by the destructive distillation of bones is treated with concentrated sulphuric acid and heated, orthophosphoric acid and calcium sulphate are produced. Calcium sulphate being insoluble is filtered off. The filtrate which contains phosphoric acid is concentrated.

$$\underset{\text{Bone ash}}{Ca_3(PO_4)_2} + 3H_2SO_4 \longrightarrow \underset{\text{ppt.}}{3CaSO_4} + 2H_3PO_4$$

(*b*) When bone ash is oxidised with concentrated nitric acid, all phosphorus present in the bone ash is converted into phosphoric acid. The resulting liquid is treated with lead acetate which precipitates insoluble lead phosphate. Phosphoric acid is then recovered from lead phosphate by treating with H_2S gas.

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$

$$2H_3PO_4\ (\textit{impure}) + 3(CH_3COO)_2Pb \longrightarrow Pb_3(PO_4)_2 + 6CH_3COOH$$

$$Pb_3(PO_4)_2 + 3H_2S \longrightarrow 3PbS + 2H_3PO_4\ (\textit{pure})$$

The acid so obtained is separated from PbS by filtration. It is concentrated by heating. Nitric acid employed in this process should not be more than 30 to 35% since higher concentration makes the reaction too violent.

Properties (*a*) **Physical.** Orthophosphoric acid forms bard, colourless (glassy) rhombic prisms. The crystals deliquesce in air and form a syrupy liquid. Commercial acid is 82.98%. It is soluble in all proportions. Its density is 1.87 and melts at 42.3°C. (anhydrous). The concentrated phosphoric acid (usually 85%) is a colourless syrupy liquid which, on being cooled in vacuum, yields crystals of anhydrous acid, H_3PO_4. The acid also forms hemihydrate, H_3PO_4. H_2O.

(*b*) **Chemical.** (*i*) *Reaction with alkalies.* It is tribasic acid and forms three series of salts with alkalies.

$$H_3PO_4 + NaOH \longrightarrow \underset{\substack{\text{Primary sodium}\\ \text{phosphate}}}{NaH_2PO_4} + H_2O$$

$$H_3PO_4 + 2NaOH \longrightarrow \underset{\substack{\text{Secondary sodium}\\ \text{phosphate}}}{Na_2HPO_4} + 2H_2O$$

$$H_3PO_4 + 3NaOH \longrightarrow \underset{\substack{\text{Tertiary sodium}\\ \text{phosphate}}}{Na_3PO_4} + 3H_2O$$

(*ii*) *Action of heat.* When heated to 250°C, it gives pyrophosphoric acid $H_4P_2O_7$

$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$

When heated to 320°C, it further loses one molecule of water giving metaphosphoric acid, HPO_3

$$H_4P_2O_7 \xrightarrow{320^\circ} 2HPO_3 + H_2O$$

When strongly heated (to red heat), it gives phosphorus pentoxide

$$3HPO_3 \xrightarrow{600^\circ\text{–}700^\circ} P_2O_5 + H_2O$$

(*iii*) *Action of bromides and iodides.* Phosphoric acid liberates hydrobromic and hydriodic acids from bromides and indides respectively.

$$3NaBr + H_3PO_4 \longrightarrow N_3PO_4 + 3HBr$$

$$3NaI + H_3PO_4 \longrightarrow Na_3PO_4 + 3HI$$

These reactions afford a very good method for the laboratory preparation of these halogen acids.

(*iv*) *Action on silver nitrate.* Silver nitrate gives a yellow precipitate of silver ortho-phosphate with ortho-phosphoric acid.

$$3AgNO_3 + H_3PO_4 \longrightarrow \underset{\text{Yellow ppt.}}{Ag_3PO_4} + 3HNO_3$$

(*v*) *Action on barium chloride.* Barium chloride gives a white precipitate of barium ortho-phosphate in neutral or slightly alkaline solution.

$$2BaCl_2 + 2H_3PO_4 \longrightarrow \underset{\text{White ppt.}}{Ba_3(PO_4)_2} + 6HCl$$

(*vi*) *Action on magnesia mixture.* Ortho-phosphoric acid reacts with magnesia mixture (*i.e.* $MgCl_2 + NH_4OH$) to give a white crystalline precipitate of ammonium magnesium phosphate, NH_4MgPO_4.

$$H_3PO_4 + MgCl_2 + NH_4OH \longrightarrow \underset{\substack{\text{White}\\ \text{crystalline}\\ \text{ppt.}}}{NH_4MgPO_4.} + 2HCl + H_2O$$

(vii) Oxidising properties. It has no oxidising properties below 350–400°C but at higher temperature it is fairly reactive towards metals and is reduced.

(viii) Acidic nature. The acid is a tribasic acid and ionises as follows :

$$H_3PO_4 \rightleftarrows H^+ + [H_2PO_4]^- \ ; \ K_1 = 7.5 \times 10^{-3}$$

$$[H_2PO_4]^- \rightleftarrows H^+ + [HPO_4]^{2-} \ ; \ K_2 = 6.2 \times 10^{-8}$$

$$[HPO_4]^{2-} \rightleftarrows H^+ + [PO_4]^{3-} \ ; \ K_3 = 1.1 \times 10^{-12}$$

The acid, therefore, forms three types of salts namely *primary phosphates* (*e.g.* NaH_2PO_4), *secondary phosphates* (*e.g.* Na_2HPO_4) and tertiary phosphates (*e.g.* Na_3PO_4).

(ix) When phosphoric acid and phosphates are treated with ammonium molybdate, $(NH_4)_2MoO_4$ and excess of conc. HNO_3, a canary yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$ is obtained, on warming to about 60°C

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\substack{\text{Canary}\\\text{yellow}\\\text{ppt.}}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Uses. *(i)* Pure ortho-phosphoric acid has pharmaceutical applications and is used in the preparation of nervous tonics. *(ii)* It serves as a stabilizer for hydrogen peroxide. *(iii)* It is used for the manufacture of fertilizers, dyes, enamels and porcelain cement. *(iv)* It is used in the dental fillings.

5. Pyrophosphoric Acid, $H_4P_2O_7$.

Preparation. It is prepared by prolonged heating of orthophosphoric acid between 200–300°C.

$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$

Properties. *(a)* **Physical.** It is a white crystalline mass with melting point 61°C. It is readily soluble in water.

(b) **Chemical.** *(i) Action on alkalies.* It is a tetra-basic acid and forms two series of salts with alkalies.

$$2NaOH + H_4P_2O_7 \longrightarrow \underset{\substack{\text{Disodium acid}\\\text{pyrophosphate}}}{Na_2H_2P_2O_7} + 2H_2O$$

$$4NaOH + H_4P_2O_7 \longrightarrow \underset{\substack{\text{Tetra sodium}\\\textit{neutral}\text{ pyro-}\\\text{phosphate}}}{Na_4P_2O_7} + 4H_2O$$

(ii) Action on silver nitrate. It gives a white precipitate of silver pyrophosphate.

$$2AgNO_3 + H_4P_2O_7 \longrightarrow \underset{\text{white ppt.}}{Ag_4P_2O_7} + 4HNO_3$$

(iii) Action on water. Pyrophosphoric acid dissolves in cold water and is slowly converted to ortho-phosphoric acid but in hot water and especially in the presence of nitric acid, it is easily converted into ortho-phosphoric acid.

$$H_4P_2O_7 + H_2O \longrightarrow 2H_3PO_4$$

(*iv*) *Acidic nature.* The acid is tetrabasic and is stronger than ortho-phosphoric acid. It ionises as :

$$H_4P_2O_7 \rightleftarrows H^+ + H_3P_2O_7^- \ ; K_1 = 1.4 \times 10^{-1}$$
$$H_3P_2O_7^- \rightleftarrows H^+ + H_2P_2O_7^{2-} \ ; K_2 = 1.1 \times 10^{-2}$$
$$H_2P_2O_7^{2-} \rightleftarrows H^+ + HP_2O_7^{3-} \ ; K_3 = 2.7 \times 10^{-7}$$
$$HP_2O_7^{3-} \rightleftarrows H^+ + P_2O_7^{4-} \ ; K_4 = 2.4 \times 10^{-10}$$

Although the acid is tetrabasic, it forms two types of salts *viz. normal salts* (*e.g.* $M_4P_2O_7$) and *diacid salts* (*e.g.* $M_2H_2P_2O_7$).

(*v*) *Action of heat.* On heating at 316°C, it gives metaphosphoric acid, HPO_3

$$H_4P_2O_7 \xrightarrow{316°C} 2HPO_3 + H_2O$$

6. Metaphosphoric Acid or Glacial Phosphoric Acid, HPO_3.

Preparation. When $(NH_4)_3 PO_4$ or H_3PO_4 or $H_4P_2O_7$ is heated to about 32°C, meta phosphoric acid is formed.

$$(NH_4)_3PO_4 \longrightarrow HPO_3 + 3NH_3 + H_2O$$
$$H_3PO_4 \longrightarrow HPO_3 + H_2O$$
$$H_4P_2O_7 \longrightarrow 2HPO_3 + H_2O$$

Properties. (*a*) **Physical.** Meta-phosphoric acid is a hard, sticky mass. The acid is, therefore, called *glacial phosphoric acid.* It dissolves in water with a cracking noise. It volatilises on heating. It melts at 384°C.

(*b*) **Chemical** (*i*) *Action on silver nitrate.* Meta phosphoric acid gives a white precipitate with silver nitrate solution forming silver meta-phosphate, $AgPO_3$.

$$AgNO_3 + HPO_3 \longrightarrow AgPO_3 + HNO_3$$

(*ii*) *Action on barium chloride.* Barium chloride gives a white precipitate in neutral or alkaline solutions.

$$BaCl_2 + 2HPO_3 \longrightarrow Ba(PO_3)_2 + 2HCl$$

The precipitate of barium phosphate is insoluble in acetic acid.

(*iii*) *Action on water.* Aqueous solution of meta-phosphoric acid is gradually converted to ortho-phosphoric acid on prolonged standing. This conversion is accelerated in the presence of acids and on heating.

$$HPO_3 + H_2O \longrightarrow H_3PO_4$$

(*iv*) The alkali meta-phosphate, $NaPO_3$, when heated with metal oxides, forms mixed phosphate. The mixed phosphates of heavy metals have characteristic colours.

$$NaPO_3 + CuO \longrightarrow NaCuPO_4$$

This reaction finds an application in the basic radical analysis as an alternative of the borax bead test. The mixed phosphates so formed are often referred to as microcosmic beads.

(*v*) Meta-phosphoric acid or its salts are not present in the form of simple molecules but are often polymerised. In the vapour phase, meta-phosphoric acid has been reported to have the formula $(HPO_3)_2$ but in solutions or in the melt, it is $(HPO_3)_n$ where $n = 3$ or 4.

(*vi*) *Acidic nature.* It is a monobasic acid and its salts are called metaphosphates.

(*vii*) Like other phosphoric acids, it also gives ammonium molybdate test.

(*viii*) Unlike other phosphoric acids, it at once coagulates albumin (white part of the egg).

7. Peroxy Phosphoric Acids.

Phosphorus forms two peroxy phosphoric acids which are analogous to peroxy sulphuric acids and are discussed below :

(A) Peroxy Monophosphoric Acid, H_3PO_5. This acid is known in solution only. It is formed by the action of 30% H_2O_2 on P_2O_5 in acetonitrile solution at a low temperature.

$$P_2O_5 + 2H_2O_2 + H_2O \longrightarrow 2H_3PO_5$$

This acid is a powerful oxidising agent and oxidises manganous salts to permanganates.

(B) Peroxy Diphosphoric Acid, $H_4P_2O_8$. This acid is prepared by the action of H_2O_2 on the excess of pyrophosphoric acid, $H_4P_2O_7$.

$$H_4P_2O_7 + H_2O_2 \longrightarrow H_4P_2O_8 + H_2O$$

Potassium salt of the acid is stable and is prepared by the electrolysis of potassium hydrogen phosphate in presence of KF. The solution of the acid oxidises aniline nitrobenzene and nitrosobenzene. In acidic solution the acid is first hydrolysed to H_3PO_5 and finally to H_2O_2.

Distinction Between Hypophosphorus Acid and Ortho, Pyro and Meta phosphoric Acids.

The various reactions showing the distinction between these acids are given below :

Reaction	Hypo-phosphorus acid (H_3PO_2)	Ortho-phosphoric acid (H_3PO_4)	Pyro-phosphoric acid ($H_4P_2O_7$)	Meta-phosphoric acid (HPO_3)
(*i*) *Magnesia mixture*	No ppt.	White ppt.	White ppt. soluble in excess reagent	No ppt.
(*ii*) *Silver nitrate*	Reduced to metallic silver (ppt.)	Yelllow ppt. of Ag_3PO_4	White ppt. of $Ag_4P_2O_7$	White gela. tinous ppt. of $AgPO_3$
(*iii*) *Barium chloride*	No action	White ppt. soluble in acetic acid	White ppt. insoluble in acetic acid	White ppt. insoluble in acetic acid
(*iv*) *Copper sulphate (solution in acid)*	Reduced to metallic copper (ppt.)	No action	No action	No action
(*v*) *Egg albumin with dil. acetic acid*	No action	No action	No action	Coagulation takes place
(*vi*) *Acidified $KMnO_4$*	Decolorises	No action	No action	No action
(*vii*) *Cadmium chloride acidified with dil. acetic acid*	No action	No action	White ppt.	No action

Salts of the Acids

1. Sodium Ammonium Hydrogen Phosphate or Microcosmic Salt, $Na(NH_4)HPO_4.4H_2O$.

This phosphate is also called microcosmic salt since it is present in the urine of the "*microcosm*" *i.e.* man. It is prepared by dissolving molecular proportion of Na_2HPO_4 and NH_4Cl in a little hot water, filtering off NaCl precipitated and crystallising.

$$Na_2HPO_4 + NH_4Cl \longrightarrow \underset{\text{In solution}}{Na(NH_4)HPO_4} + \underset{\text{ppt.}}{NaCl}$$

It forms colourless needle-like crystals. When heated strongly it loses NH_3 and water and forms a transparent glassy bead of sodium meta-phosphate, $NaPO_3$.

$$Na(NH_4)HPO_4 \xrightarrow{\Delta} NH_3 + H_2O + NaPO_3$$

This bead of $NaPO_3$ in the fused state combines with metallic oxides (*e.g.* CuO) to form coloured ortho-phosphates.

$$CuO + NaPO_3 \longrightarrow \underset{\text{Blue bead}}{CuNaPO_4}$$

The salt is used for testing SiO_2 with which a cloudy bead containing floating particles of SiO_2 is obtained.

2. Sodium Hexametaphosphate or Graham's Salt, $(NaPO_3)_n$.

It is a polymeric compound with high molecular weight (12000–18000). It is miscalled sodium hexametaphosphate. At present it is called *sodium (1 : 1) phosphate glass* and its preferred formula is Na_2O (1 : 1) P_2O_5. Graham's salt is prepared by heating NaH_2PO_4, until a molten material, $(NaPO_3)_n$ is formed. This material, on chilling, gives a glassy solid which is called Graham's salt. The changes taking place can be shown as follows :

$$NaH_2PHO_4 \xrightarrow{230°} \underset{\substack{\text{Sod. cyclo-}\\\text{triphosphate}}}{Na_2(P_3O_9)} \xrightarrow{638°} \text{Molten } (NaPO_3)_n \xrightarrow{\text{Chilling}} \text{Graham's salt (Glassy solid)}$$

Graham's salt is a transparent glassy solid. It is hygroscopic and readily soluble in water without limit. On divitrification, the material loses water. This water is regarded as being present in Graham's salt as OH groups attached to terminal phosphorus atom of a chain of PO_4 tetrahedra. Graham's salt is used for softening water. It acts by sequestering the Ca^{2+} and Mg^{2+} ions *i.e.* it forms complexes with Ca^{2+} and Mg^{2+} ions present in hard water. A hard water, after the treatment with Graham's salt, becomes soft since Ca^{2+} and Mg^{2+} ions present in it have been eliminated; hence Graham's salt is also given a trade name "*calgon*" (derived from "*calcium gone*") Graham's salt is also used with other alkalies for cleansing sinks, drain's floors etc.

Structure of the Acids

While discussing the structure of the oxy-acids of phosphorus, the following points should be kept in mind. (*i*) The structure of these acids is such that each phosphorus atom is tetrahedrally surrounded by neighbouring atoms. (*ii*) The number of H-atoms directly linked to oxygen atoms are responsible for the basicity of oxyacids. In other words we can say that the basicity of oxy-acids is determined by the number of —OH groups present in the acid. (*iii*) The hydrogen atoms directly linked to phosphorus atom are responsible for the reducing properties of the oxy-acids. The larger the number of H-atoms, the greater is the reducing property of the acid.

1. Hypophosphorus Acid, H_3PO_2.

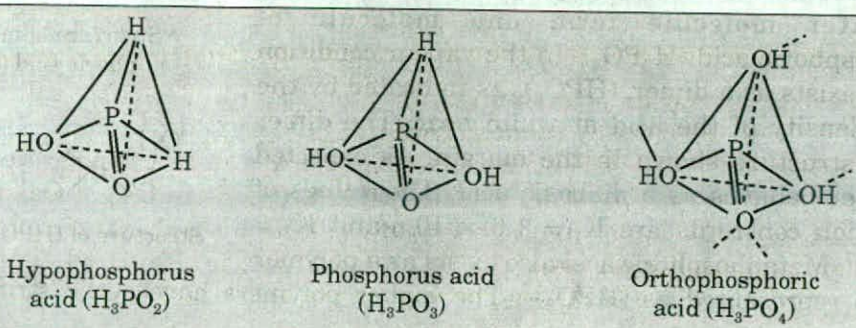
The measurement of heat of neutralisation, conductivity and hydrogen concentration have shown that the acid is a monobasic acid, *i.e.* the acid has only one —OH group attached directly to P-atom. The strong reducing character of the acid confirms the presence of P—H bonds in the molecule. In the light of these properties and the evidences obtained from Raman spectra and X-ray analysis of its salts, the structure shown in Fig. 34.3 has been assigned to this acid. Obviously it has a tetrahedral structure.

2. Phosphorus Acid, H_3PO_3.

Nuclear magnetic resonance spectroscopy of the acid, its salts and esters shows that there is one H-atom directly linked to P-atom. This H-atom is not ionisable and confers reducing properties to the acid while other two H-atoms which are ionisable exist as —OH groups. The dibasic nature of the acid has been confirmed from heat of neutralisation data. X-ray study of the crystalline acid has shown that three oxygen atoms and one of the three H-atoms are arranged tetrahedrally round P-atom. Keeping in view the above points, the acid has been assigned the tetrahedral structure shown in Fig. 34.3. This structure can be regarded as being obtained from the structure of H_3PO_2 by the replacement of one H-atom by one —OH group.

3. Orthophosphoric Acid or Phosphoric Acid, H_3PO_4.

It is a *tribasic acid* and forms the ester, trietheyl phosphate $PO(OC_2H_5)_2$. On this basis, the acid has been assigned the tetrahedral structure shown in Fig. 34.3. In this structure tetrahedral PO_4 groups are connected together by hydrogen bonds which have been shown by dotted lines (......)



Hypophosphorus acid (H_3PO_2)

Phosphorus acid (H_3PO_3)

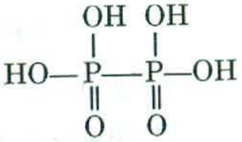
Orthophosphoric acid (H_3PO_4)

Fig. 34.3. Tetrahedral structures of hypophosphorus acid (H_3PO_2), phosphorus acid (H_3PO_3) and orthophosphoric acid (H_3PO_4). In the structure of H_3PO_4 acid the dotted lines ...... show the hydrogen bonds.

Structures of various orthophosphate anions can be derived easily from the structure of orthophosphoric acid by the step-wise removal of H-atom from OH groups. The tetrahedral structures of H_3PO_2, H_3PO_3 and H_3PO_4 acids can be explained on the basis of sp^3 hybridisation of P-atom.

4. Hypophosphoric Acid, $H_4P_2O_6$.

The double formula of the acid, $H_4P_2O_6$ has been indicated by the molecular weight determination of the acid and its salts, and by the diamagnetic nature of its salts. The acid has been given the structure shown in the margin. This structure is supported by the Raman spectrum, X-ray studies of diammonium hypophosphate, the absence of reducing properties and tetrabasic nature of the acid. Due to its tetrabasic nature four H-atoms are bonded to O-atoms.



Structure of hypophosphoric acid, $H_4P_2O_6$

5. Pyrophosphoric Acid, $H_4P_2O_7$.

It is a *tetrabasic acid* and hence has the structure shown in Fig. 34.4. This structure follows directly from the fact that this acid can be prepared by removing one H_2O molecule from two molecules of orthophosphoric acid (H_3PO_4) which has tetrahedral shape.

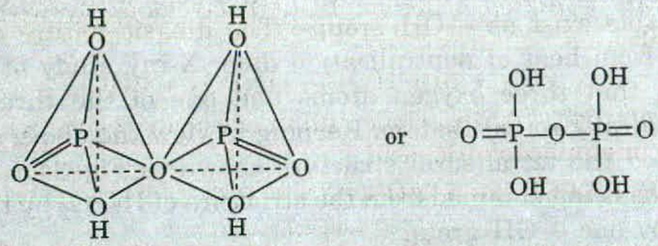
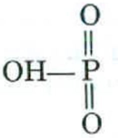


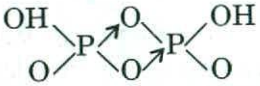
Fig. 34.4. Structure of pyrophosphoric acid, $H_4P_2O_7$.

6. Metaphosphoric Acid, HPO_3.

It is a *monobasic acid* and hence has the structure shown in the margin. This structure is also supported by the fact that the acid can be prepared by eliminating one water molecule form one molecule of orthophosphoric acid (H_3PO_4). In the vapour condition the acid exists as a dimer, $(HPO_3)_2$ as indicated by the vapour density of the acid at white heat. The dimer has the structure shown in the margin. As expected this dimer behaves as a diabasic acid. The values of dissociation constants are $K_1 = 1.6 \times 10^{-2}$ and $K_2 = 7.0 \times 10^{-7}$. Metaphosphoric acid also exists as a polymer which is represented as $(HPO_3)_n$. The higher polymers have cyclic structures.



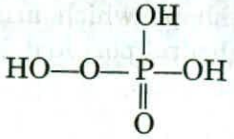
Structure of metaphosphoric acid (HPO_3)



Structure of $(HPO_3)_2$ dimer

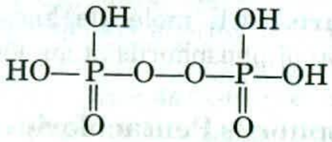
7. Peroxy phosphoric Acids.

Both the peroxy-phosphoric acids namely H_3PO_5 and $H_4P_2O_8$ have the following structures.



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

Peroxy-monophosphoric acid, H_3PO_5



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

Peroxy-diphosphoric acid, $H_4P_2O_8$

Halides

With halogens phosphorus forms two types of halides *viz. trihalides*, PX_3 and *pentahalides*, PX_5. Diphosphorus tetrachloride, P_2Cl_4 and diphosphorus tetraiodide, P_2I_4 are also known. Here we shall discuss only PCl_3 and PCl_5.

1. Phosphorus Trichloride. PCl_3

Preparation. The trichloride of phosphorus is obtained by passing dry chlorine over red phosphorus gently heated in a retort over a water bath. The trichloride formed distils over and is collected in a receiver cooled in a freezing mixture.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

Properties. (*a*) **Physical.** PCl_3 is a colourless liquid which fumes strongly in air. Its density is 1.57. It boils at 76°C.

(*b*) **Chemical.** (*i*) *Action of water.* PCl_3 reacts violently with water forming phosphorus acid.

$$PCl_3 + 3HOH \longrightarrow H_3PO_3 + 3HCl$$

(*ii*) *Action of conc. H_2SO_4.* Conc. sulphuric acid reacts with PCl_3 forming chlorosulphonic metaphosphoric acid.

$$4H_2SO_4 + 2PCl_3 \longrightarrow \underset{\text{Chlorosulphonic acid}}{2HSO_3.Cl} + P_2O_5 + 2SO_2 + 4HCl + H_2O$$

(*iii*) *Action of Cl_2.* PCl_3 reacts with chlorine forming phosphorus pentachloride.

$$PCl_3 + Cl_3 \longrightarrow PCl_5$$

(*iv*) *Action of sulphur trioxide.* It reacts with SO_3 forming phosphoryl chloride and sulphur dioxide.

$$SO_3 + PCl_3 \longrightarrow POCl_3 + SO_2$$

(*v*) *Action of thionyl chloride ($SOCl_2$).* It reacts with $SOCl_2$ forming phosphoryl chloride, thio-phosphoryl chloride and phosphorus pentachloride.

$$SOCl_2 + 3PCl_3 \longrightarrow POCl_3 + PSCl_3 + PCl_5$$

(*vi*) *Action of organic compounds.* It reacts with all such organic compounds which contain an alcoholic group forming corresponding chloro derivatives. Thus —OH group is replaced by —Cl. For example :

$$\underset{\text{Ethyl alcohol}}{3C_2H_5OH} + PCl_3 \longrightarrow \underset{\text{Ethyl chloride}}{3C_2H_5Cl} + H_3PO_3$$

$$\underset{\text{Benzene sulphuric acid}}{3C_6H_5SO_2.OH} + PCl_3 \longrightarrow \underset{\text{Benzene sulphonly chloride}}{3C_6H_5SO_2.Cl} + H_3PO_3$$

Uses. PCl_3 is used in the preparation of organic compounds.

Structure. PCl_3 molecule has a pyramidal shape which arises from sp^3 hybridisation of phosphorus atom. One of the tetrahedral positions is occupied by a lone pair.

2. Phosphorus Pentachloride, PCl_5.

Preparation. Phosphorus pentachloride is prepared by the action of dry chlorine (*excess*) on phosphorus trichloride.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

Properties. (*i*) It is an almost colourless crystalline solid with pungent odour when pure.

(*ii*) On heating, it sublimes below 100°C and can be melted (m.pt. = 148°) only by heating under pressure.

(*iii*) *Dissociation.* It is inferred from its vapour density data that phosphorus pentachloride dissociates on heating into phosphorus trichloride and free chlorine.

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

(*iv*) *Action of water.* It combines with H_2O violently forming phosphorus oxychloride, $POCl_3$ (with insufficient water) and phosphoric acid, H_3PO_4 (with excess of water).

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

(*v*) *Action of hydroxy compounds.* It reacts with hydroxy compounds and replaces the hydroxyl groups by chlorine atoms. For example :

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + PCl_5 \longrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3 + HCl$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

$$\underset{\text{Sulphuric acid}}{SO_2(OH)_2} + 2PCl_5 \longrightarrow \underset{\text{Sulphuryl chloride}}{SO_2Cl_2} + 2POCl_3 + 2HCl$$

(*vi*) *Action of concentrated sulphuric acid.* Sulphuric acid forms chlorosulphonic acid.

$$H_2SO_4 + PCl_5 \longrightarrow POCl_3 + HCl + \underset{\text{Chlorosulphonic acid}}{Cl.SO_3H}$$

(*vii*) *Action of boric acid (H_3BO_3).* Boric acid forms its anhydride and boron trioxide with PCl_5.

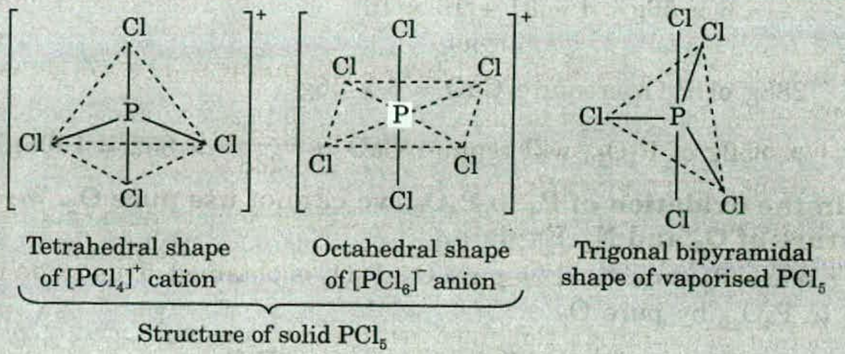
$$2H_3BO_3 + 3PCl_5 \longrightarrow 3POCl_3 + 6HCl + B_2O_3$$

(*viii*) *Action of metals.* Many metals like Zn, Cd, Au, Pt etc. are converted into chlorides when heated with PCl_5.

$$PCl_5 + Zn \longrightarrow PCl_3 + ZnCl_2$$

Uses. It is extensively used in organic chemistry for replacement of hydroxy groups for chlorine atoms, *i.e.* it is used as a chlorinating agent in organic chemistry.

Structure. X-ray studies have shown that solid PCl_5 consists of ionic lattice of tetrahedral $[PCl_4]^+$ cations and octahedral $[PCl_6]^-$ anions. (*See* Fig. 34.5). In the *vapour state* PCl_5 consists of descrete PCl_5 molecules which have a trigonal bipyramidal shape. (*See* Fig. 34.5). The axial P—Cl distance = 2.19A° and equatorial P—Cl = 2.04A°. *The axial bonds are relatively weak and have considerable ionic character.*



Tetrahedral shape of $[PCl_4]^+$ cation

Octahedral shape of $[PCl_6]^-$ anion

Trigonal bipyramidal shape of vaporised PCl_5

Structure of solid PCl_5

Fig. 34.5. Shape of PCl_5 in the solid and vaporised state.

Oxy-halides

All the oxy-halides of the POX_3(X = F, Cl and Br) are known. These compounds are also called *phosphoryl halides*. Here we shall discuss only $POCl_3$.

Preparation. It is prepared by the action of water on phosphorus pentachloride or by heating PCl_5 with oxalic acid or boric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$PCl_5 + H_2C_2O_4 \longrightarrow POCl_8 + HCl + CO_2 + CO$$

$$3PCl_5 + 2H_3BO_3 \longrightarrow 3POCl_3 + B_2O_3 + 6HCl$$

Properties. It is a colourless liquid (b. pt. = 107.2°, m.pt. = 1.37°). With water, it forms orthophosphoric acid.

$$POCl_2 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

It reacts with organic compounds containing hydroxyl group.

$$3ROH + POCl_3 \longrightarrow 3RCl + H_3PO_4$$

Structure. $POCl_3$ molecule has a *tetrahedral shape* with oxygen atom occupying one of the tetrahedral positions (See Fig. 34.6).

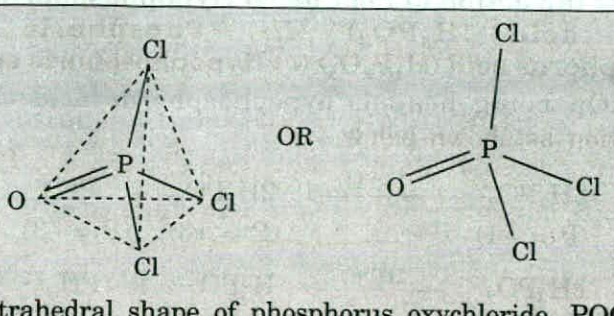


Fig. 34.6. Tetrahedral shape of phosphorus oxychloride, $POCl_3$.

Questions with Answers

[A] Questions on Oxides

Q.1 How many grams of CaO are required to nutralize 852g of P_4O_{10}?

Ans : The chemical equation for the reaction is :

$$\begin{array}{lll} 6CaO \quad + & P_4O_{10} & \longrightarrow \quad 2Ca_3(PO_4)_2 \\ 6 \times 56g & 4 \times 31 + 10 \times 16 & \\ & = 288g & \end{array}$$

288g of P_4O_{10} require CaO = 6 × 56g

$$\therefore \text{ 852g of } P_4O_{10} \text{ will require CaO} = \frac{6 \times 56}{288} \times 852 = \mathbf{1008g}$$

Q.2 In the oxidation of P_4 to P_4O_6, we cannot use pure O_2. We actually use mixture of O_2 and N_2. Explain.

Ans : When P_4 is oxidised by pure O_2, P_4O_6 is obtained. This oxide is further oxidised to P_4O_{10} by pure O_2.

$$P_4 \xrightarrow{+3O_2} P_4O_6 \xrightarrow{+2O_2} P_4O_{10}$$

In order to prevent the oxidation of P_4O_6 to P_4O_{10}, we use mixture of N_2 and O_2 in place of pure O_2.

$$P_4 + 3O_2 \ (\textit{Containing } N_2) \longrightarrow P_4O_6$$

Q.3 Oxides of nitrogen have open chain structures while those of phoshphorus have closed chain or cage structures. Explain your answer with one example of each type of oxides.

or The oxides of phosphorus have cage structres and not open ones. Explain.

Ans : Since N-atom has smaller size and higher electronegativity than P-atom, this atom forms $p\pi - p\pi$ multiple bonds easily with O-atom and hence oxides of N have open chain structure. On the other hand, since P-atom has larger size and lower electronnegativity than N-atom, this atom does not form $p\pi - p\pi$ multiple bonds with O-atoms. Thus oxides of P-atom donot have open chain structure. P-atom prefers to form single bonds with O-atoms. This tendency of phosphorus gives closed chain or cage sturcture to its oxides. For example N_2O_5 which is an oxide of N has open chain structure but P_4O_6 and P_4O_8 (oxides of P) have closed chain structures.

[B] Questions on Oxy acids

Q.1 Discuss the action of heat on (*i*) Hypophosphorus acid (H_3PO_2) (*ii*) Phosphorus acid (H_3PO_3) (*iii*) Phosphoric acid (H_3PO_4). (*iv*) Pyrophosphorus acid ($H_4P_2O_5$) (*v*) Hypophosphoric acid ($H_4P_2O_6$).

Ans : (*i*) On being heated, hypophosphorus acid (H_3PO_2) undergoes disproportionation as shown below :

$$\begin{array}{lcll} 3H_3PO_2 & \xrightarrow{140°C} & 2H_3PO_3 \ + & PH_3 \\ (P = +1) & & (P = +3) & (P = -3) \end{array}$$

$$\begin{array}{lcll} 2H_3PO_2 & \xrightarrow{160°C} & H_3PO_4 \ + & PH_3 \\ (P = +1) & & (P = +5) & (P = -3) \end{array}$$

(*ii*) On heating, phosphorus acid (H_3PO_3) undergoes disproportionation (*self oxidation-reduction reaction*)

$$\underset{(P\,=\,+3)}{4H_3PO_3} \xrightarrow{160^\circ C} \underset{(P\,=\,+5)}{3H_3PO_4} + \underset{(P\,=\,-3)}{PH_3}$$

(*iii*) When H_3PO_4 is heated, different products are obtained. The nature of products obtained depends on the temperature.

$$2H_3PO_4 \xrightarrow[(-H_2O)]{250^\circ C} H_4P_2O_7 + H_2O$$

$$H_3PO_4 \xrightarrow[(-H_2O)]{600^\circ C} HPO_3 + H_2O$$

$$2H_3PO_4 \xrightarrow[(-H_2O)]{\text{Red heat}} P_2O_5 + 3H_2O$$

(*iv*) On heating strongly, $H_2P_2O_5$ gives metaphosphorus acid (HPO_2).

$$H_4P_2O_5 \xrightarrow[(-H_2O)]{\text{Strong heating}} 2HPO_2 + H_2O$$

(*v*) (*a*) On being heated above its m.pt; $H_4P_2O_6$ undregoes disproportionation to phosphorus acid (H_3PO_3) and metaphosphoric acid (HPO_3)

$$H_4P_2O_6\ (P = +4) \xrightarrow[m.pt.]{\text{Heat above}} H_3PO_3\ (P = +3) + HPO_3\ (P = +5)$$

(*b*) On heating at about 180°C, the acid gives orthophosphoric acid (H_3PO_4), metaphosphoric acid (HPO_3) and phosphene (PH_3)

$$4H_4P_2O_6 \xrightarrow{\text{Above } 180^\circ} 3H_3PO_4 + 4HPO_3 + PH_3$$

Q.2 What happens when :

(*i*) Phosphoric acid is heated with HNO_3 and ammonium molybdate.

(*ii*) Phosphoric acid reacts with $Ca_5(PO_4)_3F$. **(*I.I.T. 1998*)**

(*iii*) Hypophorus acid reacts with NaOH solution.

Ans : (*i*) On heating H_3PO_4, in presence of HNO_3, with ammonium molybdate [$(NH_4)_2MoO_4$], a canary yellow ppt. of ammonium phosphomolybdate $(NH_4)_3PO_4.12MoO_3$ is formed.

$H_3PO_4 + 21HNO_3 + 12(NH_4)_2MoO_4 \rightarrow 21NH_4NO_3 + 12H_2O +$

$(NH_4)_3PO_4.12\ MoO_3$ (*yellow ppt. of ammonium phosphomolybdate*)

(*ii*) HF is formed.

$Ca_5(PO_4)_3F + 7H_3PO_4 + 5H_2O \rightarrow 5Ca(H_2PO_4)_2.\ H_2O + HF$

(*iii*) Hypophorus acid is H_3PO_2. Since this acid is a monobasic acid, only one H-atom will be replaced by Na-atom. Thus NaH_2PO_2 will be formed.

$$\begin{array}{l} H_3PO_2 \rightarrow H^+ + H_2PO_2^- \\ NaOH \rightarrow Na^+ + OH^- \\ \hline H_3PO_2 + NaOH \rightarrow Na^+H_2PO_2^- + H_2O \end{array}$$

Q.3 What is the difference between the structure of NO_3^- and PO_3^- ions.

Ans : NO_3^- ion (nitrate ion) exists in the free state. Since N-atom in this ion is sp^2 hybridised, NO_3^- ion has trigonal planar shape with ONO bond angle equal to 120° as shown in Fig. 34.7

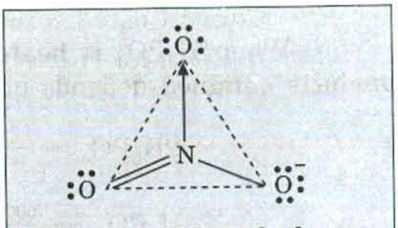


Fig. 34.7 Trigonal planar structure of NO_3^- ion

On the other hand PO_3^- ion (metaphosphate ion) does not exist in the free state, since experiments have shown that this ion gets polymerised and forms polymerised ion, $[(PO_3^-)_n]^{n-}$. Thus PO_3^- ion exists as a polymerised ion, $[(PO_3^-)_n]^{n-}$ which is called *polymeric metaphosphate ion*. $[(PO_3^-)_n]^{n-}$ ion has polymeric structure which may be either linear structure or cyclic structure as shown below in Fig. 34.8 and Fig. 34.9.

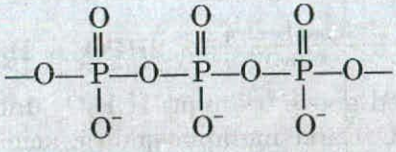
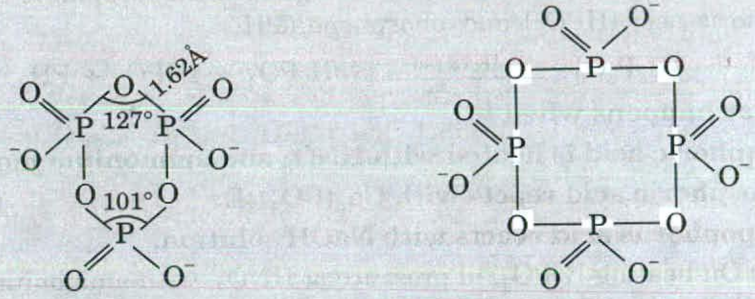


Fig. 34.8 Linear structure of polymeric metaphosphate ion, $[(PO_3^-)_n]^{n-}$



(*a*) Cyclic structure of trimetaphosphate ion, $[(PO_3)_3]^{3-}$

(*b*) Cyclic structure of tetrametaphosphate ion, $[(PO_3)_4]^{4-}$

Fig. 34.9 Cyclic structres of trimetaphosphate and tetrametaphosphate ions.

In these polymetaphosphate ions, various PO_3^- units are linked together through P – O – P bonds. In these PO_3^- units, P-atom is sp^3 hybridised and thus each PO_3^- unit has tetrahedral shape. It may also be seen that for getting cycilc metaphosphate the minimum value of $n = 3$. Thus $(PO_3^-)_3$ is the smallest cyclic metaphosphate ion This cyclic metaphosphate ion [*i.e.* $(PO_3^-)_3$] has three P–O–P bonds.

Q.4 Explain the following, giving appropriate reason for your answer.

(*i*) Orthophosphorus acid is not tribasic though it contains three H-atoms. ***(I.I.T.1987)***

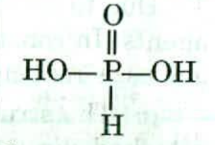
(*ii*) Orthophoric acid is tribasic but phosphorus acid is dibasic. ***(I.I.T. 1982)***

(*iii*) Concentrated solution of orthophosphoric acid is syrupy liquid.

(*iv*) H_3PO_2 and H_3PO_3 act as reducing agents but H_3PO_4 does not.

(*v*) H_3PO_3 (Phosphorus acid) is diprotic (or dibasic).

Ans : (*i*) Orthophoshorus acid (H_3PO_3) is not tribasic acid, since it contains only two OH groups attached directly with central P-atom or since it contains only two H-atoms bound to O-atoms or since it contians only two ionisable H-atoms as is evident from its structure. Due to the presence of two OH groups H_3PO_3 dissociates in two stages given below :



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-OH$$

Structure of ortho-phosphorus acid molecule, H_3PO_3

$$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^-$$
$$H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-}$$

It is due to the presence of two OH groups in H_3PO_3 molecule that it behaves as a dibasic acid and not as a tribasic acid.

(*ii*) The aqueous solution of orthophosphoric acid (H_3PO_4) ionises in three stages and hence gives three types of anions.

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ (*Dihydrogen phosphate ion*)

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ (*Hydrogen phosphate ion*)

$HPO^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ (*Phospahte ion*)

Due to the production of three types of anions, H_3PO_4 gives three types of salts. Due to the formation of three types of salts, H_3PO_4 is tribasic. Its tribasic nature is also confirmed by the fact that H_3PO_4 has three OH groups attached directly with P-atom

Although phosphorus acid (H_3PO_3) has three H-atoms, its aqueous solution gives only two H^+ ions on ionisation

$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^-$ (*Dihydrogen phosphite ion*)

$H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-}$ (*Hydrogen phosphite ion*)

Due to the production of two H^+ ions, H_3PO_3 behaves as a dibasic acid. Its dibasic character is also confirmed by the fact that H_3PO_3 has only two OH groups attached directly with P-atom.

(*iii*) The solid and concentrated solution of orthophosphoric acid has various H_3PO_4 tetrahedral molecules connetced together by H-bonds (Fig. 34.10). The existence of H-bonds between different tetrahedral H_3PO_4 molecules increases the viscosity of the concentrated solution of the acid and thus accounts for the syrupy nature of the acid. H-bonds have been shown by dotted lines.

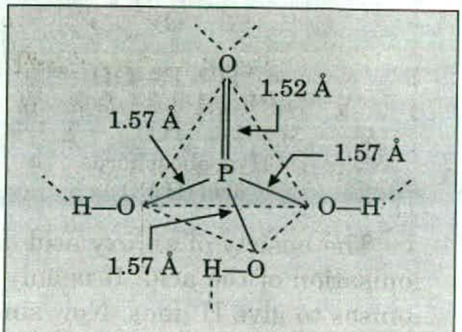
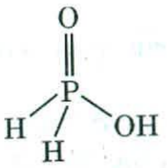
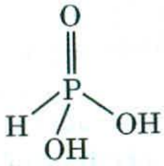


Fig. 34.10 Structure of H_3PO_4 in solid and concentarted solution form.

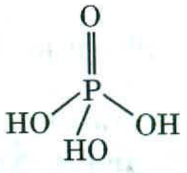
(*iv*) The structures of H_3PO_2, H_3PO_3 and H_3PO_4 are :



Hypophosphorus acid (H_3PO_2)



Phosphorus acid (H_3PO_3)



Orthophosphoric acid (H_3PO_4)

Due to the presence of P – H bonds, both H_3PO_2 and H_3PO_3 act as reducing agents. In constrast, H_3PO_4 does not have any P – H bond and hence it does not act as a reducing agent.

(*v*) The structure of H_3PO_3 molecule shows that it contains two – OH groups attached directly with the central P-atom. Thus H_3PO_3 ionises to give two H^+ ions and hence is dibasic.

$$\begin{array}{l} H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^- \\ H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-} \\ \hline H_3PO_3 \rightleftharpoons 2H^+ + HPO_3^{2-} \end{array}$$

Q.5 How will you get the following from orthophoric acid : (*i*) yellow phosphorus (*ii*) metaphophoric acid.

Ans : (*i*) $H_3PO_4 \xrightarrow[(-H_2O)]{600°C} HPO_3 + H_2O$

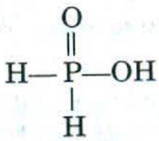
HPO_3 obtained as above is mixed with powered coke and distilled in fireclay retorts at a bright red heat. Coke reduces HPO_3 to phosphorus and is itself oxidised to CO.

$4HPO_3 + 10C \rightarrow P_4 + 10CO + 2H_2O$

(*ii*) $H_3PO_4 \xrightarrow[(-H_2O)]{600°C} HPO_3$ (*Meta phosphoric acid*) + H_2O

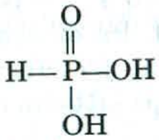
Q.6 Predict whether the basicity of H_3PO_2, H_3PO_3 and H_3PO_4 is the same or different. Give reasons for your answer.

Ans : The structure of the given molecules are given below :



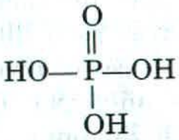
$$H-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-OH$$

Hypophosphorus acid (H_3PO_2)



$$H-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH$$

Orthophosphorus acid (H_3PO_3)



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

Orthophosphoric acid (H_3PO_4)

The basicty of an oxy acid depends on the number of H^+ ions obtained by the ionisation of the acid. It is only OH group (*s*) attached to the central atom which ionises to give H^+ ions. Now since H_3PO_2, H_3PO_3 and H_3PO_4 molecules have one, two and three OH groups attached with central P-atom, these molecules, on ionisation, give one, two and three H^+ ions. Thus these acids have differnt bascity.

Q.7 How will you obtain pyrophosporic acid from calcium phosphate.

Ans : This can be obtained as follows :

$$\underset{\text{Cal. phosphate}}{Ca(PO_4)_2} + 3H_2SO_4(conc.) \longrightarrow CaSO_4 + 2H_3PO_4$$

$$2H_3PO_4 \xrightarrow[(-H_2O)]{250°C} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} + H_2O$$

[C] Questions on Halides.

Q.1 What is the structure of PCl_5 molecule in the solid state.

Ans : In the solid state PCl_5 exists as an ionic compound which can be represented as $[PCl_4]^+ [PCl_6]^-$ in which the cation, PCl_4^+ is tetrahedral and the anion, PCl_6^- is octahedral.

Q.2 Give the structure of PBr_5 and PI_5 molecules in the solid state.

Ans : In the solid state PBr_5 exists as an ionic solid whose structure is $[PBr_4]^+ Br^-$. The cation, $[PBr_4]^+$ has tetrahedral geometry. Similary PI_5 molecule also exists as an ionic solid, $[PI_4]^+ I^-$ in which the cation, $[PI_4]^+$ has tetrahedral geometry.

Q.3 P–X bonds in PX_5 molecules (X = F, Cl) are not of the same length. Explain.

Ans : In PX_5 molecules, P-atom is sp^3d hybridised. In this molecule, each of the two axial P – X bonds.is slightly larger than each of the three equatorial P – X bonds. The difference in bond lengths is because of the following reasons :

(*i*) sp^3d hybridisation gives trigonal bipyramidal geometry to PX_5 molecule. This geometry is not a symmetrical geometry, since two bond angles are of 90°, three bond angles are of 120° and one bond angle is of 180°. Due to unsymmetrical trigonal bipyramidal geometry of PX_5 molecule, all P – X bonds are not of the same length.

(*ii*) All the P – X bonds are not of the same length, since axial X-atoms experience greater repulsion as compared to that experienced by equatorial X-atoms.

Q.4 PCl_5 acts a chlorinating agent in organic reactions. Why ?

Ans : In the gaseous and liquid states, PCl_5 molecule has a trigonal bipyramidal shape in which the two axial P – Cl bonds are slightly larger in length than the three equatonal P – Cl bonds. Due to the difference in bond lengths, PCl_5 becomes unstable and hence dissociates to give two Cl-atoms making axial bonds.

$$PC_5 \rightleftharpoons PCl_3 + Cl_2$$

Due to the production of Cl_2, PCl_5 acts as a chlorinating agent.

Q.5 Can PCl_5 act as an oxidising agent (OA) or as a reducing agent (RA). Give appropriate reasons for your answer.

Ans : Maximum oxidation state (O.S.) shown by P-atom is +5 which is shown by this elements in PCl_5. Thus :

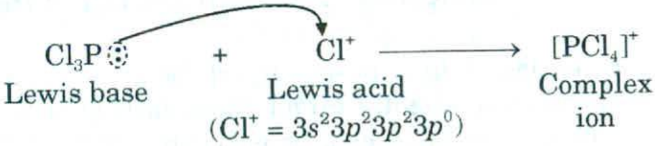
(*i*) If PCl_5 (P = +5) acts as an OA, then it would be reduced to some compound in which P-atom would show an O.S. lower than +5. This is possible as is evident from the following reactions :

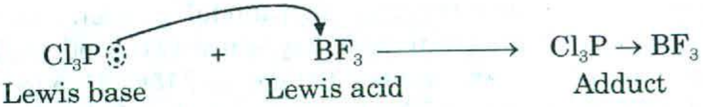
$$\begin{array}{ccccccc} 2Ag & + & PCl_5 & \longrightarrow & 2AgCl & + & PCl_3 \\ (Ag = 0) & & (P = +5) & & (Ag = +1) & & (P = +3) \\ Sn & + & 2PCl_5 & \longrightarrow & SnCl_4 & + & 2PCl_3 \\ (Sn = 0) & & (P = +5) & & (Sn = +4) & & (P = +3) \\ H_2 & + & PCl_5 & \longrightarrow & HCl & + & PCl_3 \\ (H = 0) & & (P = +5) & & (H = +1) & & (P = +3) \end{array}$$

(*ii*) If PCl_5 (P = +5) acts as a RA, then it would be oxidised to some other compound in which P-atom would show an O.S. higher than +5. This is not possible because maximum O.S. shown by P-atom is only +5.

Q.7 Which one of PCl_3 and PCl_5 is a better Lewis acid ?

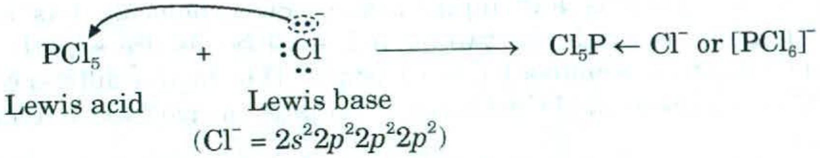
Ans : The central P-atom in PCl_3 molecule has a *lp* of electrons and hence PCl_3 molecule acts as a Lewis base and not as a Lewis acid. Lewis base character of PCl_3 molecule is evident from the following reactions.





$[PCl_4]^+$ ion is found in the solid state of PCl_5 (solid $PCl_5 \equiv [PCl_4]^+ [PCl_6]^-$)

In PCl_5 molecule, since central P-atom does not have *lp* of electrons, this molecule does not show basic character. However, since P-atom has vacant *d*-orbitals, PCl_5 molecule shows acidic character. The acidic character is evident from the following reaction.



$[PCl_6]^-$ ion is found in PCl_5 when PCl_5 is in the solid state. (Solid $PCl_5 \equiv [PCl_4]^+ [PCl_6]^-$)

Above discussion shows that PCl_5 is a Lewis acid but PCl_3 is a Lewis base.

Q.6 PCl_5 is known but PI_5 is unkown. Why ?

Ans : Since Cl-atoms are smaller in size, these atoms can easily be accomdated round P-atom to from PCl_5. On the other hand, since I-atoms are larger in size, these atoms cannot be accomdated round P-atom and hence PI_5 cannot be formed.

Q.7 Which is more stable PCl_5 or PCl_3 ?

Ans : PCl_3 is more stable than PCl_5 because on heating PCl_5 decomposes to form PCl_3 and Cl_2.

$$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$$

Q.7. When PCl_5 is heated, it is broken to form PCl_3 and Cl_2. Expalin this reaction.

Ans : We know that in PCl_5 molecule, due to greater (*bp* – *bp*) repulsions, the two axial P – Cl bonds are less stable than the three equatorial P – Cl bonds. It is for this reason that when PCl_5 is heated, less stable axial bonds are removed from PCl_5 molecules as Cl_2.

$$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$$

University Questions

1. Explain the formulae and structures of various oxides of phosphorus. (*Delhi 87; Punjab 84*)
2. Write a note on "oxy-acids of phosphorus". (*Jiwaji 83, 84*)
3. What are polymetaphosphates? (*Madras 86*)
4. Give brief account of the chlorides of phosphorus. (*Madras 86*)
5. Describe the action of heat on orthophosphorus acid. Give balanced chemical equation. (*Delhi 99*)
6. H_3PO_3 is dibasic acid whereas H_3PO_4 is a tribasic acid. Explain. (*Gorakhpur 99*)
7. Describe the method of preparation and uses of hypophosphorus acid. (*Allahabad 99*)
8. (*a*) Name the oxyacids of phosphorus and write down their structural formulae.
   (*b*) Discuss the basicity and reducing character of these acids. (*Lucknow 2000*)

CHAPTER

35

General Characteristics of Group 16 (VI A) Elements : Oxygen Group Elements

Group VI A of the periodic table consists of five elements *viz. Oxygen* (O), *Sulphur* (S), *Selenium* (Se), *Tellurium* (Te) *and Polonium* (Po). Oxygen and sulphur are the *typical elements* of this group. The elements O, S, Se and Te are often collectively called *chalcogens*, *i.e.* the ore forming elements.

Position of Oxygen Group Elements in the Periodic Table

The inclusion of the elements of Group VI A in the same sub-group of the periodic table is justified by the following general characteristics of these elements.

I. Electronic Configurations.

The electronic configurations of the atoms of these elements are : O(Z = 8) $\rightarrow$ 2, 6 ($2s^2p^4$); S(Z = 16) $\rightarrow$ 2, 8, 6 ($3s^2p^4$); Se(Z = 34) $\rightarrow$ 2, 8, 18, 6 ($4s^2p^4$); Te(Z = 52) $\rightarrow$ 2, 8, 18, 18, 6 ($5s^2p^4$); Po(Z = 84) $\rightarrow$ 2, 8, 18, 32, 18, 6($6s^2p^4$). It is clear that all the elements have ns^2p^4 configuration in the outermost shell. The four electrons in *p*-orbitals are distributed as $p_x^2 p_y^1 p_z^1$ in accordance with *Hund's rule*. The penultimate shell in oxygen atom contains s^2 group (*saturated*), in sulphur s^2p^6 (*saturated*), in selenium $s^2p^6d^{10}$ (*saturated*), whereas in tellurium and polonium $s^2p^6d^{10}$ (*unsaturated*). This shows that oxygen differs from sulphur and these two elements from the remaining elements of this group. We thus conclude that the elements of this group are *p*-block elements.

II. Similarities in Physical Properties and Gradation in Them.

Some of the physical properties of these elements are discussed below :

1. Density, Atomic Volume, Melting and Boiling Point. With the rise of atomic number the *density*, the *atomic volume*, *the melting point* and the *boiling point* all show a steady increase. Polonium shows exception when we consider its melting and boiling points. Due to diminished availability of *s* electron pair, the melting and boiling point of Po are less than those of Te. The large difference in melting and boiling points between O and S is attributed, in part, to the fact that whereas oxygen exists in the form of O_2 molecules, sulphur exists as S_8 molecules.

2. Ionisatian Energies. Due to the increased nuclear charge, the first and subsequent ionisation energies of these elements are higher than the corresponding elements of group VA. These elements have high values of ionisation energies. These high values indicate that the elements of this group show reluctance to lose the electrons to form positive ions. As the size of the atom increases, the values of ionisation energies decrease down the group.

3. Metallic and Non-metallic Character. Due to the decrease of ionisation energy from oxygen to polonium, the metallic character of these elements increases down the group. For example oxygen and sulphur are distinctly non-metallic and some of the metallic properties begin to develop in selenium and tellurium Polonium which is radioactive is definitely a metal.

4. Atomicity. (*Molecular structure*). All the elements are polymeric. Oxygen molecule is diatomic molecule (O_2) while the molecules of other elements are more complex, *e.g.* sulphur, selenium and polonium are *octatomic molecules viz.* S_8, Se_8 and Po_8 with *puckered ring structures.* These structures contain 8-atom rings or zig-zag chains. In these staggered rings 8-atoms are joined together by covalent bonds. The tendency of these elements to exist in 8-atom rings is greatest with sulphur and decreases as we go down the group. Such type of structure accounts for oxygen being as gas and the other members being solids. Puckered ring structure of sulphur molecule, S_8 is shown in Fig. 35.1. Such rings give molecular crystal in which the rings are held together by relatively weak polar forces. Consequently both the forms of sulphur (rhombic or mono-clinic forms) have low melting points.

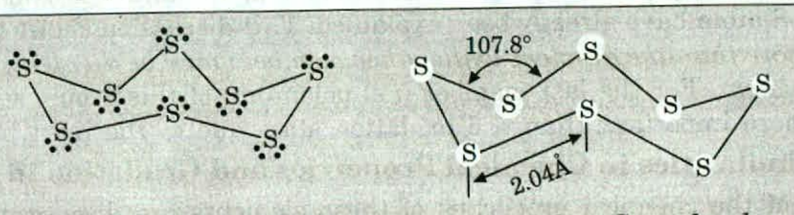


Fig. 35.1. Puckered ring structure of sulphur S_8 molecule.

5. Polymorphism. (*Allotropy*). All the elements are polymorphic, *i.e.* they show allotropy, *e.g.* oxygen exists in two nonmetallic forms *viz.* O_2 and O_3. Sulphur has several allotropic forms all of which are non-metallic, *e.g. rhombic*, *monoclinic* and *plastic sulphur*. Se has two forms: *red* (*non-metallic*) and *grey* (*metallic*). Te exists in two forms *non-metallic and metallic* (more stable), Po also exists in two forms α and β (*both metallic*).

6. Catenation. Oxygen and to a greater extent sulphur shows the property of catenation *i.e.* they have a tendency to form chains of identical atoms *e.g.* chains of sulphur atoms are present in persulphides, polythionic acids and in S_8 molecule. Oxygen gives polyoxides similar to poly sulphides given by sulphur. Examples are : H_2O_2, H—O—O—H; H_2S_2, H—S—S—H; H_2S_3, H—S—S—S—H; H_2S_4, H—S—S—S—S—H.

7. Oxidation States. Since all the elements of this group have ns^2p^4 configuration in their outermost orbit, they attain noble gas configuration *viz.* ns^2p^6 either by gaining or by sharing two electrons. Thus these elements show two types of oxidation states.

(*a*) Negative oxidation states. The high electronegativity of oxygen indicates that it will tend to complete its octet preferably by gaining electrons. These shared electrons, for the purpose of determining the oxidation state, will be counted towards oxygen because it forms the electronegative atom in all its compounds (excepting, of course, OF_2 molecule in which oxygen is as O^{2+} ion).

Hence most of the metal oxides have O^{2-} ions and are ionic, giving oxygen an oxidation state equal to –2.

The electronegativities of S, Se and Te are low and hence their compounds even with most electropositive elements will not be more than 50% ionic. As a result the formation of S^{2-}, Se^{2-} and Te^{2-} ions is less probable. The least electronegative element Po does not form Po^{2-} but it forms Po^{2+}.

(b) Positive oxidation states. Oxygen, being highly electronegative, shows only –2 oxidation state in its compounds, *i.e.* does not show positive oxidation state, except in OF_2. As we move down the group, electronegativity decreases and the tendency of the elements to show the positive oxidation state increases. S, Se, Te and Po can also show, in addition to + 2 oxidation state, + 4 and + 6 oxidation states. This is due to the availability of *d*-orbitals in these elements. Oxygen atom has no *d*-orbital and hence cannot show + 4 and + 6 oxidation states. In case of sulphur unpairing of electrons can take place, if the promotion of 3*p* and 3*s* electrons is made to 3*d* orbitals. + 2, + 4 and + 6 oxidation states in case of S-atom have already been explained. This discussion shows that *oxygen is never more than the divalent while other members may be divalent, tetravalent and hexavalent.* For the last member (*i.e.* polonium) of this group, + 4 oxidation state is more important than + 6 oxidation state due to the inert pair effect.

III. Similarities in Chemical Properties and Gradation in Them.

Some of the chemical properties of these elements are discussed below :

1. Formation of Hydrides. All the elements of this group form the hydrides of H_2M type, where M = O, S, Se, Te and Po.

Preparation. H_2O is prepared by burning H_2 in the atmosphere of O_2 while H_2S, H_2Se and H_2Te are prepared by the action of acids on metal sulphides, selenides and tellurides, *e.g.*

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

$$K_2Se + H_2SO_4 \longrightarrow K_2SO_4 + H_2Se$$

H_2Po has been prepared only in traces by dissolving Mg foil plated with Po in 0.2 N HCl.

Properties. (*i*) **Physical state.** Water is a colourless, odourless liquid while the hydrides of other elements are colourless, poisonous gases with unpleasant odours. These are inflammable gases which burn with a blue flame.

(*ii*) **Volatility.** The volatility of these hydrides increases markedly from H_2O to H_2S and then decreases. Abnormal low volatility of H_2O (*i.e.*, high boiling point) is due to its association as a result of hydrogen bonding both in solid and liquid states. As a consequence H_2O has the highest boiling point and melting point among the hydrides as shown here : $H_2O = 100°, 0.0°$; $H_2S = -60.3°, -85.5°$; $H_2Se = -41.3°, -65.7°$; $H_2Te = -23°, -51.0°$. The former numbers indicate the boiling points (in °C) while the later number indicate the melting points (in °C). Due to lower electronegativity of S-atom, H-bonding in H_2S is rare and hence the association of H_2S molecules does not occur, but H_2S gas remains as unassociated molecule. This makes H_2S to have more volatility than H_2O. In going down the group, the volatility of H_2M hydrides decreases as $H_2S \rightarrow H_2Se \rightarrow H_2Te$ due to the increase in molecular weights of the hydrides.

***(iii)* Thermal stability and reducing power.** The thermal stability of the hydrides decreases from H_2O to H_2Te. Thus water dissociates at about 2000°C, H_2S at 400–600°C, H_2Se at about 150°C while H_2Te decomposes even at ordinary temperature. The decrease in thermal stability from H_2O to H_2Te is because the size of M^{2-} ion in H_2M hydrides increases from O^{2-} to Te^{2-} ion and hence the charge is distributed over a large volume and this makes the H_2M hydride thermally unstable. The decrease in thermal stability from H_2O to H_2Te is also because of an increase in M—H bond length as we move from H_2O to H_2Te as shown here : H_2O, 0.96A°; H_2S, 1.32A°; H_2Se, 1.47A°, H_2Te, 1.73A° The increase of M—H bond length from O—H (in H_2O) to Te—H (in H_2Te) weakens the M—H bond and hence the hydride becomes thermally unstable. With the decrease of thermal stability of these hydrides from H_2O to H_2Te, the reducing power of these hydrides gradually increases in the same direction.

***(iv)* Covalent character.** Since the electronegativity of O, S, Se and Te decreases from O to Te, the electronegativity difference between M (M = O, S, Se, Te) and H decreases and hence the ionic character of M—H bond also decreases from O—H to Te—H bonds in H_2M hydrides. In other words *the covalent character of these hydrides increases from H_2O to H_2Te.*

The increase in covalent character from H_2O to H_2Te can also be explained by Fajan's rules. According to one of these rules as the size of M^{2-} ion in H_2M hydrides increases from O^{2-} to Te^{2-}, the tendency of these ions to form covalent hydrides increases.

***(v)* Acidic character.** Aqueous solutions of the hydrides of these elements behave as weak, diprotic acids and hence ionise as :

$$\begin{array}{l} H_2M \rightleftharpoons H^+ + HM^- \\ HM^- \rightleftharpoons H^+ + M^{2-} \\ \hline H_2M \rightleftharpoons 2H^+ + M^{2-} \end{array}$$

The acidic character of these acids increases in the sequence from H_2O to H_2Te. The increase in acidic character from H_2O to H_2Te is also confirmed by the fact that the value of dissociation constant of these hydrides also increases in the same direction as shown here : $H_2O = 1.0 \times 10^{-11}$, $H_2S = 1.1 \times 10^{-7}$, $H_2Se = 2.0 \times 10^{-4}$, $H_2Te = 2.3 \times 10^{-3}$. As the charge density on the conjugate bases *viz.* OH^-, SH^-, SeH^- and TeH^- decreases from OH^- to TeH^-, the proton is less tightly held with higher members and hence the acidic character increases from H_2O to H_2Te.

***(vi)* Shape of H_2M hydrides and HMH bond angles.** All these hydrides have *V-shape* (*i.e.* angular or bent shape). In these molecules the central atom (M atom) is sp^3 hybridised. Out of the four sp^3 hybrid orbitals two have lone pairs of electrons while the remaining two have bonding electron pairs. Although the spatial arrangement of the electron pairs is tetrahedral round the central M atom, due to the presence of two lone pairs in the two hybrid orbitals, the shape of MH_2 hydrides gets distorted and becomes *V-shape*.

Due to the distortion in shape, HMH bond angle in all the hydrides is never equal to the ideal tetrahedral angle (= 109.5°), but less than this value. HMH bond angles are as : $H_2O = 104.5°$, $H_2S = 92.5°$, $H_2Se = 91.0°$, $H_2Te = 90.0°$. The decrease in HMH bond angle from H_2O to H_2Te has been explained on the basis of the concept of electronegativity values of the central atom (M atom).

2. Formation of Halides. All the elements of this group form binary halides. Since fluorine is more electronegative than oxygen, fluorine compounds with oxygen are called *fluorides of oxygen* rather than *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 Cl, Br and I are called oxides of these halogens rather than halides of oxygen, *e.g.*, ClO_2 is called *chlorine dioxide* rather than *dioxygen chloride*. Important halides are discussed below :

(A) Hexafluorides (MF_6). Except oxygen, all other elements form hexa fluorides. In these fluorides the element (S, Se or Te) shows its maximum covalency of six by using its *d*-orbitals. These can be prepared by the direct combination of the elements. Hexafluorides are relatively stable and their stability decreases from SF_6 to TeF_6 due to the increase in size from S to Te atoms. Thus SF_6 is extremely stable and inert both thermally and chemically. SeF_6 is quite reactive (*i.e.* less stable) while TeF_6 is still more reactive as is evident from the fact that TeF_6 is completely hydrolysed by H_2O and adds F^- ion and other Lewis bases like $(CH_3)_3N$ to form 8-coordinated complex.

$$TeF_6 + 6H_2O \longrightarrow 6HF + H_2TeO_6$$

$$TeF_6 \xrightarrow{+F^-} [TeF_7]^- \xrightarrow{+F^-} [TeF_8]^{2-}$$

$$TeF_6 + 2(CH_3)_3N \longrightarrow \underset{\text{Adduct}}{TeF_6.\ 2(CH_3)_3N}$$

All the hexafluorides are colourless gases. All have low boiling points and hence show a degree of covalency. All the hexafluorides have *regular octahedral geometry* which results from *sp^3d^2* hybridisation of the central atom, M(M = S, Se or Te). All the M—F bonds are σ-bonds. All the FMF bond angles and M—F bond lengths are equal. The octahedral shape of SF_6 molecule on the basis of *sp^3d^2* hybridisation has already been explained. Of all the hexafluorides, SF_6, due to its chemical inertness and high value of dielectric constant, is industrially important, since it is used as a gaseous insulator in high voltage generators.

(B) Tetrahalides (MX_4). Preparation. PTetrafluorides cannot be prepared by the direct reaction between the element and F_2, since this reaction gives hexafluorides. Rather these are obtained by indirect methods like those given below :

$$S + 4CoF_3 \longrightarrow SF_4\ (g) + 4CoF_2$$

$$SeCl_4 + 4AgF \longrightarrow SeF_4\ (l) + 4AgCl$$

$$TeO_2 + 2SeF_2 \longrightarrow TeF_4\ (s) + 2SeOF_2$$

Tetrachlorides, tetrabromides and tetraiodides are prepared by the direct reaction between the element and X_2 molecule.

$$M + 2X_2 \longrightarrow MX_4$$

$$(M = S, Se, Te)$$

Properties (*i*) *Physical state.* Among the tetrafluorides SF_4 is a gas, SeF_4 is a liquid while TeF_4 is solid. Among the tetrachlorides SCl_4 is an unstable liquid while $SeCl_4$ and $TeCl_4$ are solids. TeI_4 is a dark grey powder and PoI_4 is a black solid.

(*ii*) *Thermal stability.* Tetrafluorides are more stable to thermal decomposition than tetrahalides. $TeCl_4$ is more stable than SCl_4 and $SeCl_4$. $SeBr_4$ is unstable and dissociates into Se_2Br_2 and Br_2.

$$2SeBr_4 \longrightarrow Se_2Br_2 + 3Br_2$$

$SeBr_4$ is also readily hydrolysed as :

$$SeBr_4 + 4H_2O \longrightarrow H_2SeO_3 + H_2O + 4HBr$$

(*iii*) *Fluorinating property.* All the tetrafluorides are strong fluorinating agents.

(*iv*) *Lawis acid.* Tetrafluorides can act as strong Lewis acid, since they can accept electrons and are converted into hexafluorides. For example :

(*a*) SF_4 reacts with F_2 and is converted into SF_6. SeF_4 and $TeCl_4$ combine with F^- and Cl^- ions respectively to form complex ions.

$$SF_4 + F_2 \longrightarrow SF_6;\ TeCl_4 \xrightarrow{+\ 2Cl^-} [TeCl_6]^{2-}$$

$$SeF_4 \xrightarrow{+\ F^-} [SeF_5]^- \xrightarrow{+\ F^-} [SeF_6]^{2-}$$

(*b*) Both SF_4 and SeF_4 form solid 1 : 1 addition compounds with BF_3, AsF_5 and SbF_5 which act as Lewis bases in these reactions.

(*v*) *Structure.* All the tetrahalides (MX_4) possess see-saw geometry which can be regarded as a distorted trigonal bipyramidal structure having one lone pair (*lp*) of electrons in the basal (*i.e.* equatorial) position of the trigonal bipyramid. The structure of SF_4 molecule (in the gaseous state) has already been explained. See-saw geometry of MX_4 molecules arises due to the sp^3d hybridisation of the central atom (M atom). The distortion in shape is due to the presence of one lone pair of electrons. Lone pair occupies the equatorial position of the trigonal bipyramid, since in this case the *lp—lp* repulsion in minimum. In MX_4 molecule the two axial M—X bonds are slightly bent towards the equatorial M—X bonds, showing the repulsion effect of lone pair. The axial M—X bonds are longer than the equatorial M—X bonds.

(C) Dihalides (MX_2). Only oxygen forms difluoride (OF_2). Excepting oxygen, all the remaining elements form dichlorides (SCl_2, $SeCl_2$, $TeCl_2$, $PoCl_2$). Excepting oxygen and sulphur, all other elements form dibromides ($SeBr_2$, $TeBr_2$, $PoBr_2$). None of the elements forms diodides. SCl_2 is prepared by saturating S_2Cl_2 with Cl_2 at room temperature and $PoCl_2$ is prepared by reducing $PoCl_4$ with [illegible] $TeBr_2$ is prepared by reacting tellurium with Br_2. $SeCl_2$ and $SeBr_2$ are unstable and decompose in the vapour state. The stability of dihalides decreases from SX_2 to SeX_2 and that of the dihalides of the same element decreases from MCl_2 to MBr_2. Thus : $SCl_2 > SeCl_2 > TeCl_2 > PoCl_2$; $SeCl_2 > SeBr_2$; $TeCl_2 > TeBr_2$; $PoCl_2 > PoBr_2$. All the dihalides (MX_2) possess *angular* (*V-shaped*) structure which is similar to that of H_2O molecule. The angular structure can be regarded as a distorted tetrahedral structure having two lone pairs of electrons. The angular structure of MX_2 molecules arises due to sp^3 hybridisation of the central atom (M atom). The distortion in shape is due to the presence of two lone pairs of electrons. As an example, the structure of SCl_2 molecule is explained as follows :

The Lewis dot structure of SCl_2 molecule is $Cl—\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}—Cl$ which shows that the central atom (*i.e.* S-atom) uses two of its six valence-shell electrons ($S \rightarrow 3s^2p^4$) in forming two S—Cl σ-bonds while the remaining four electrons (*i.e.* two electron pairs) remain as non- bonding electrons on S-atom. Thus σ-*bps* = 2 and *lps* = 2 and hence σ-*bps* + *lps* = 2 + 2 = 4. Now since the sum of σ-*bps* and *lps* is 4, S-atom in SCl_2 molecule is supposed to be sp^3 hybridised. Out of the four sp^3 hybrid orbitals, two contain *lps* while each of the remaining two has one electron. These two singly-filled sp^3 hybrid orbitals make a head-to-head (linear) overlap with the singly-filled $3p_x$ orbitals on each of the two Cl-atoms ($Cl \rightarrow 3s^2, 3p_x^{\ 1}\ 2p_y^{\ 2}\ 3p_z^{\ 2}$) and form two sp^3 (S)—$2p$ (Cl) σ-bonds as shown in Fig. 35.2.

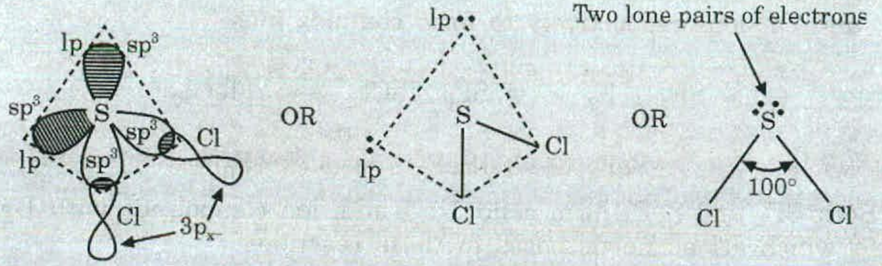


Fig. 35.2. Pictorial representation of the formation of two σ-bonds in SCl_2 molecule (σ-*bps* = 2, *lps* = 2) which has angular shape (V-shape).

Although the spatial arrangement of four electron pairs (*bps* = 2 and *lps* = 2) round the central S-atom is tetrahedral, duo to the presence of two lone pairs of electrons in two hybrid orbitals, the shape of SCl_2 molecule gets distorted and becomes V-shape and Cl—S—Cl bond angle decreases from the expected tetrahedral angle (= 109.5°) to 103°. The distortion in shape and the decrease in bond angle can be explained on the basis of same reasoning as used in case of H_2O molecule. Bond angles in case of OF_2 and $TeBr_2$ dihalides are 103° and 98° respectively.

(D) Dimeric monohalides (M_2X_2). The well known dimeric monohalides are O_2F_2, S_2F_2, S_2Cl_2, S_2Br_2, Se_2F_2, Se_2Cl_2, Se_2Br_2. S_2Cl_2 is prepared by the action of dry Cl_2 on molten sulphur

$$2S + Cl_2 \longrightarrow S_2Cl_2$$

The dimeric monohalides are slowly hydrolysed and undergo disproportionation. For example :

$$2S_2F_2 + 2H_2O \xrightarrow{\text{Hydrolysis}} 4HF + SO_2 + 2S$$

$$\underset{(Se\ =\ +1)}{2Se_2Cl_2} \xrightarrow{\text{Disproportionation}} \underset{(Se\ =\ +4)}{SeCl_4} + \underset{(Se\ =\ 0)}{3Se}$$

O_2F_2 and S_2Cl_2 molecules, like H_2O_2 molecule, have *non-linear* and *non-planar* structures (Fig. 35.3) in which the two O—F and S—Cl bonds are asymmetrically distributed, *i.e.* all the four atoms in both the molecules are lying in different planes.

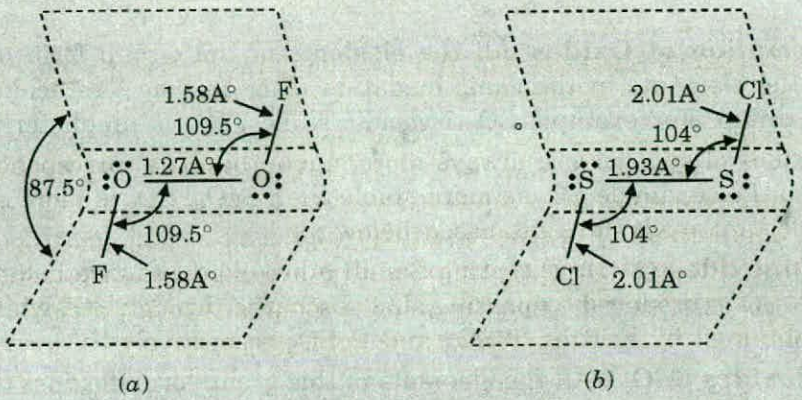


Fig. 35.3. Non-linear and non-planar structures of (*a*) O_2F_2 and (*b*) S_2Cl_2 molecules.

Each of the two O-atoms in O_2F_2 molecule and each of the two S-atoms in S_2Cl_2 molecule has two lone pairs of electrons on it. Thus each O-atom in O_2F_2 and each S-atom in S_2Cl_2 molecule is sp^2 hybridised. How O—O and O—F bonds in O_2F_2, and S—S and S—Cl bonds in S_2Cl_2 are formed has been shown in Fig. 35.4.

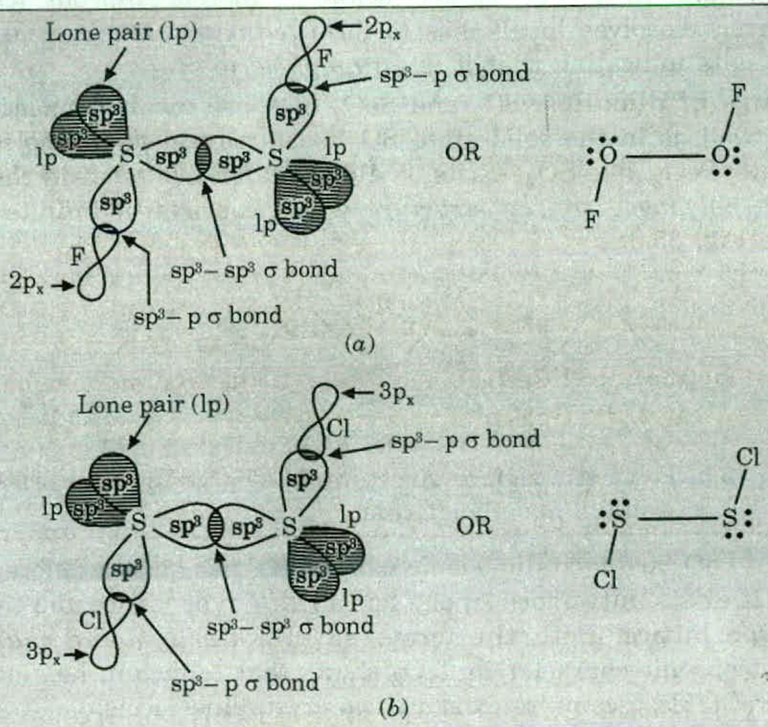


Fig. 35.4 Pictorial representation of the formation of (*a*) O—O and O—F bonds in O_2F_2, and (*b*) S—S and S—Cl bonds in S_2Cl_2 molecules. Each of the shaded sp^3 hybrid orbital contains a lone pair of electrons.

In O_2F_2 molecule it appears that the ionic forms also contribute with the covalent form.

$$\underbrace{F{-}O^{+} = OF^{-},\ F^{-}O = O^{+} - F}_{\text{Ionic forms}} \qquad \underset{\text{Covalent form}}{F{-}O{-}O{-}F}$$

3. Formation of Oxides. All the elements of this group form oxides. The oxides of the elements in the same oxidation state become less acidic as we go down the group. For example SO_2 is acidic while TeO_2 is amphoteric.

The oxides of sulphur are always more stable than the corresponding oxides of selenium. For example SO_2 is more stable than SeO_2. SO_3 is more stable than SeO_3. Important oxides are discussed below :

(A) Monoxides (MO). Excepting Se, all other elements give monoxides (SO, TeO, PoO). SO is produced by passing slow discharge through SO_2 while TeO and PoO are obtained by heating $TeSO_3$ and $PoSO_3$ respectively.

(B) Dioxides (MO_2). All the elements of this group form dioxides (SO_2, SeO_2, TeO_2, PoO_2). These oxides can be prepared by burning the elements in air.

These oxides differ from one another in their reaction towards H_2O. Gaseous SO_2 dissolves in H_2O giving *sulphurous acid* (H_2SO_3) which is known in solution only. SeO_2 gives an acidic aqueous solution which on evaporation in vacuum gives *selenous acid* (H_2SeO_3) in colourless hexagonal prisms. The formation of H_2SO_3 and H_2SeO_3 indicate that SO_2 and SeO_2 both are *acidic* in nature. TeO_2 is almost insoluble in H_2O giving very dilute solution of *tellurous acid* (H_2TeO_3), TeO_2, however, dissolves in alkalies to form *tellurites*, $MTeO_3$ and in acids to form basic salts indicating that it is an *amphoteric oxide.*

Structure of dioxides. SO_2 and SeO_2 both are covalent molecules. In the gaseous as well as in the solid state SO_2 exists as a discrete molecule. In the gaseous state, SeO_2, like SO_2, exists as a discrete molecule but in the solid state SeO_2 has a *polymeric zig-zag structure* which consists of infinite non-planar chains (See Fig. 35.5).

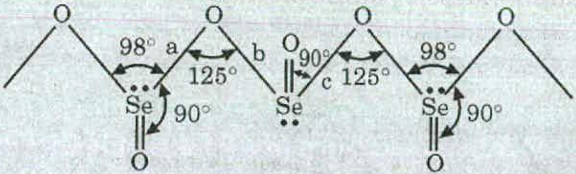
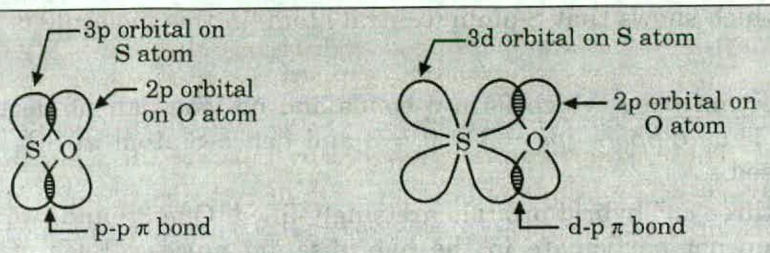


Fig. 35.5. Polymeric zig-zag structure of solid SeO_2 which consists of infinite non-planar chains, $a = b = c = 1.78A°$.

TeO_2 and PoO_2 are crystalline *ionic solids.* TeO_2 has quite a different structure from SeO_2. It exists in two forms : one has a *rutile* type lattice and the other has *brookite* type lattice. Both the forms have *distinctly ionic character.* The development of ionic character in TeO_2 shows that tellurium has more metallic character. PoO_2 also seems to exist in two crystalline forms.

Structure and shape of SO_2 molecule. The structure of this molecule is $O = \underset{\bullet\bullet}{S} = O$ which shows that S-atom (central atom) in this molecule is surrounded by two σ-*bps* and one *lp*. Thus σ-*bps* + *lp* = 2 + 1 = 3 and hence S-atom is sp^2 hybridised.

One of the three sp^2 hybrid orbitals is occupied by a lone pair of electrons while the remaining two have one electron each. One 3*p* orbital and one 3*d* orbital on S-atom do not participate in the hybridisation process. Each of the two singly-filled sp^2 hybrid orbitals overlaps with the singly-filled 2*p* orbitals on both O-atoms and form two σ-bonds while 3*p* and 3*d* orbitals on S-atom make a sidewise overlap with 2*p* orbitals on both O-atoms and form *p—p* and *d—p* π-bonds respectively. The sidewise overlap of 3*p* orbital on S-atom with 2*p* orbital on O-atom to form *p—p* π bond and that between 3*d* orbital on S-atom with 2*p* orbital on O-atom to form *d—p* π bond is shown in Fig. 35.6.



(*a*) (*b*)

Fig. 35.6. Formation of (*a*) *p—p* and (*b*) *d—p* π bonds in SO_2 molecule.

Although the arrangement of three electron pairs (two electron pairs used in σ-bonds and one lone pair) round S-atom is triangular, due to the presence of one lone pair of electrons on S-atom, the shape of SO_2 molecule gets distorted and becomes *angular* (V-shape) (Fig. 35.7) OSO bond angle has been found to be equal to 119.5° which is nearly equal to 120°. This value of bond angle and the polar nature of SO_2 molecule confirms its angular geometry. The formation of *p—p* and *d—p* π bonds in SO_2 molecule results in bringing S-and O-atoms closer to each other and hence the S—O bond length becomes shorter than the single S—O bond length. The shortening of S—O bond lengths suggests multiple bonding between S and O-atoms. The difference in the nature of π-bonds between S- and two O-atoms must mean that both S—O bond lengths must be different from each other. Actually both the bonds are of the same length. Their same length is due to the resonance between the two structures shown in the margin.

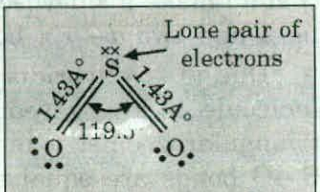
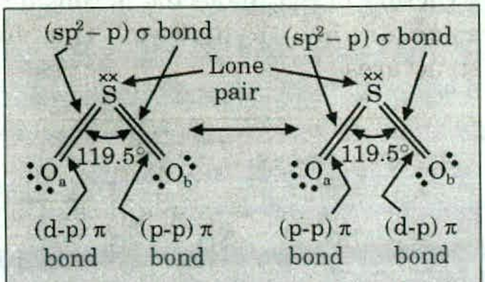


Fig. 35.7. Angular geometry of SO_2 molecule.

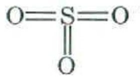


Resonance structures of SO_2 molecule

Since one of the sp^2 hybrid orbitals on S-atom is occupied by a lone pair of electrons and also since the (*lp—bp*) repulsion is more than (*bp—bp*) repulsion, OSO bond angle gets reduced from 120° to 119.5°.

(C) Trioxides (MO_3). Preparation. S, Se and Te also form the trioxides of MO_3 type (SO_3, SeO_3, TeO_3). SO_3 is prepared by catalytic oxidation of SO_2 with air, SeO_3 is formed by passing an electric discharge through selenium vapours and O_2 at 4 mm pressure while TeO_3 is made by heating telluric acid, H_6TeO_6 strongly.

Properties. SO_3 and SeO_3 are soluble in water and give sulphuric (H_2SO_4) and selenic (H_2SeO_4) acids. Thus these are acidic oxides. TeO_3 is practically insoluble in water due to the diminished tendency of Te to form multiple bonds with oxygen and its lower electronegativity resulting in greater polarity in Te—O bond. It is for this reason that TeO_3 is polymeric and insoluble in water.

Structure and Shape of SO_3 molecule. The structure of SO_3 molecule is  $O{=}\underset{\underset{O}{\|}}{S}{=}O$ which shows that S-atom (central atom) in this molecule is surrounded by three electron pairs which form σ-bonds and no lone pair of electrons is left on S-atom. Thus σ-*bps* + *ips* = 3 + 0 = 3 and hence S-atom in SO_3 molecule is sp^2 hybridised.

All the three sp^2 hybrid orbitals are singly-filled. One 3*p* and two 3*d* orbitals on S-atom do not participate in the hybridisation process. Each of the singly-filled sp^2 hybrid orbitals overlaps with the singly-filled 2*p*-orbitals on all the three O-atoms and form three sp^2 (S)—*p* (O) σ-bonds while 3*p* and 3*d* orbitals on S-atom make a sidewise overlap with 2*p* orbitals on three O-atoms and form one *p*—*p* and two *d*—*p* π bonds.

Due to sp^2 hybridisation of S-atom, SO_3 molecule in the gaseous state has planar triangular geometry in which all the three S—O bonds are equal to 1.43Å and all the OSO bond angles are equal to 120° (See Fig. 35.8).

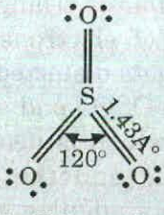
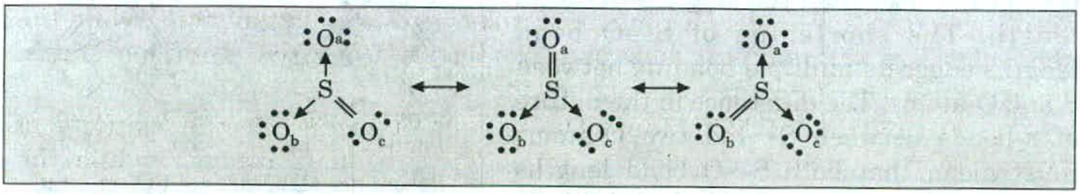


Fig. 35.8. Triangular planar geometry of SO_3 molecule in the gaseous state.

According to another view, the true structure of SO_3 molecule is considered to be a resonance hybrid of the following structures :



Solid SO_3 has either a puckered cyclic (or ring) trimeric structure (α-form) or a chain (or layer) structure (β- and γ-forms) as shown below in Fig. 35.9. SO_3 chain is made up of linked SO_4 tetrahedra. Each tetrahedron shares two oxygen atoms.

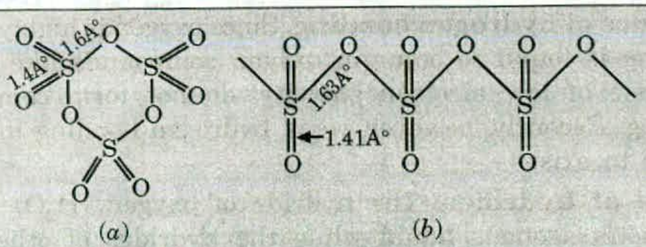


Fig. 35.9. Structure of solid SO_3 (a) Puckered ring trimeric structure (α-form) (b) Chain (or layer) structure (β- and γ-forms).

(D) Heptoxide (S_2O_7). It is only sulphur which gives heptoxide, S_2O_7. It is formed by passing a silent electric discharge in a mixture of SO_2 and O_2.

$$4SO_2 + 3O_2 \longrightarrow 2S_2O_7$$

It liberates O_2 from H_2O

$$2S_2O_7 + 4H_2O \longrightarrow 4H_2SO_4 + O_2$$

4. Formation of Oxy-acids. Sulphur, selenium and tellurium form a number of oxy acids. Out of these oxy-acids, those of sulphur are the most important and have been discussed in chapter 36.

Anomalous Properties of Oxygen : Dissimilarities with Other Elements of Group VI A.

Oxygen, the first element of group VI A, like carbon (group IV A) and nitrogen (group V A) differs considerably from the rest of the elements of group VI A because of the following inherent characteristics of oxygen : (*i*) *Small size* (*ii*) *Higher electrontgativity* (*iii*) *Non-availability of d-orbitats in the electronic configuration of oxygen atom.* The main points of difference between oxygen and the remaining members of group VI A are given below :

(*i*) Physical state. Oxygen is a *gas* while the other members are *solids.*

(*ii*) Abundance. Oxygen is the *most abundant* of all the elements and constitutes 46-6% of the earth's crust.

(*iii*) Atomicity. Oxygen molecule is *diatomic* (O_2) while the molecules of the other elements are more complex, *e.g.* sulphur and selenium have *octatomic* molecules (*i.e.* S_8 and Se_8) with puckered ring structures.

(*iv*) Oxidation states. Oxygen does not show any positive oxidation state except in oxygen difluoride, OF_2 in which it shows + 2 oxidation state, while the other members of this group show both positive and negative oxidation states. Positive oxidation states are more frequent.

(*v*) Formation of M^{2-} ions. On account of higher electronegativity of oxygen atom, *dinegative anion* O^{2-} (*oxide anion*) is more common while the S^{2-}, Se^{2-} and Te^{4-} ions are less probable.

(*vi*) Maximum covalency. The maximum covalency of oxygen is two because of the absence of *d*-orbitals in its valence-shell. Other elements, on the other hand, exhibit a maximum covalency of *six* due to the presence of *d*-orbitals in which *s*- and *p*-electrons can be promoted and thus can be made unpaired.

(vii) **Existence of hydrogen bonding.** Since oxygen is highly electronegative, hydrogen bonding is found to occur in oxygen compounds like H_2O etc. Other elements, because of low electronegativity, do not form compounds having hydrogen bonding. Recently, however, weak hydrogen bonding involving sulphur has been proved to exist.

(viii) **Nature of hydrides.** The hydride of oxygen (H_2O) is a colourless, odourless and non-poisonous liquid while the hydrides of other elements are inflammable gases with an unpleasant smell and are poisonous.

(ix) **Magnetic behaviour.** Oxygen shows paramagnetic behaviour.

(x) **Reactivity.** Metals like Cu, Ag, Hg etc. show lesser tendency to react with O_2 to form oxides than with sulphur to form sulphides. This is because of the fact that a stronger bond is formed when larger S^{2-} ion is polarised by the small Cu^{2+}, Ag^+, Hg^{2+} ions. It is because of this reason that in nature weaker metals tend to occur as sulphides rather than as oxides.

Comparison of Oxygen and Sulphur.

These are the typical elements of group VI A and show many similar and dissimilar properties.

(A) Similarities. (*i*) Both are non-metals (*ii*) They have six electrons in their outermost shell ($O_8 \rightarrow 2, 6$; $S_{16} \rightarrow 2, 8, 6$) (*iii*) It shows analogy with sulphur in compounds like (*a*) C_2H_5OH and C_2H_5SH (*b*) CO_2 and CS_2 (*b*) $(C_2H_5)_2O$ and $(C_2H_2)_2S$ (*d*) H_2O and H_2S (*iv*) O and S combine with H_2 to form the hydrides *viz.* H_2O and H_2S (*v*) They both form oxides of RO_2 type. *e.g.* O_3 ($O\ O_2$) and SO_2. (*vi*) Both the elements are obtained by heating their higher oxides and sulphides.

$$2BaO_2 \longrightarrow 2BaO + O_2 \uparrow \; ; \; FeS_2 \longrightarrow FeS + S \downarrow$$

(*vii*) They combine with carbon on heating to give CO_2 and CS_2.

(B) Dissimilarities. (*i*) O_2 is colourless and odourless gas while sulphur is a pale yellow solid with a faint odour, (*ii*) Oxygen is more widely distributed in nature than sulphur, (*iii*) Maximum covalency of oxygen is 2 while that of sulphur is 6 (*iv*) Oxygen does not react with conc. HNO_3 while sulphur is oxidised by conc. HNO_3. (*v*) Oxygen, due to non-availability of *d*-orbitals, does not form co-ordination compounds while S gives a large number of co-ordination compounds.

Conceptual Questions with Answers

Q.1 Arrange the following elements as directed :

(i) **Po, Se, Te, S and O in the increasing order of their metallic character.**

Ans : O < S < Se < Te < Po

(ii) **Po, Se, Te, S and O in the decreasing order of their ionisation energy.**

Ans : O > S > Se > Te > Po

Q.2 Explain the following :

(i) **Liq. O_2 sticks to magnet pole but liq. N_2 does not.**

Ans : O_2 is paramagnetic but N_2 is diamagnetic. Hence O_2 is attracted towards magnet but N_2 is not.

***(ii)* Sulphur exhibits greater tendency for catenation than selenium.**

Ans : As we move from S to Se, the atomic size increases and hence the strength of M–M bond decreases. As a result, S–S bond is much stronger than Se–Se bond and consequently S shows greater tendency for catenation than selenium.

***(iii)* Oxygen forms diatomic molecules (O_2) while sulphur forms octaatomic molecules (S_8).**

Ans : Due to small size of oxygen, the non-bonding electrons on the two oxygen atoms in O–O bond strongly repel each other while such repulsions are much less in S S bond. As a result O — O bond dissociation energy is much less than S — S bond dissociation energy. In other words, sulphur has much higher tendency for catenation than oxygen. Further, oxygen because of its small size has a high tendency to form $p\pi - p\pi$ multiple bonds but sulphur because of its bigger size normally does not form $p\pi - p\pi$ S = S multiple bonds.

Thus, oxygen because of its less tendency for catenation and higher tendency for $p\pi - p\pi$ multiple bonds form stable diatomic (O_2) molecules whereas sulphur because of its higher tendency for catenation and lesser tendency for $p\pi - p\pi$ multiple bonds forms octaatomic (S_8) molecules having eight membered puckered ring structure.

***(iv)* Oxygen is diatomic (O_2) and gaseous in nature while sulphur is a solid.**

Ans : The oxygen molecule is diatomic involving a double bond. Its small size produces weak intermolecular forces amongst its molecules and is, thus, a gas at room temperature. Sulphur is incapable of forming π-bonds. Its molecule has a puckered ring structure of eight sulphur atoms joined by single covalent bonds. The intermolecular forces acting between S_8 molecules are stronger and hence, sulphur is a solid.

***(v)* The tendency of the elements from S to Po to show –2 oxidation state diminishes on moving down the group from S to Po.**

Ans : Since the electronegativity of the elements decreases on moving down the group from S to Po, the tendency of these elements to accept two electrons to form M^{2-} ions which have stable noble gas configuration ($ns^2\ np^6$ configuration) also decreases. Due to the decrease in this tendency, the tendency of the elements to show –2 oxidation state also decreases. Thus since Po is the least electronegative, this element does not show –2 oxidation state.

***(vi)* Oxygen generally exhibits an oxidation state of –2 only while other members of its family show oxidation states of +2, +4 and +6 as well.**

Ans : The valence-shell of O-atom has six electrons ($O = 2s^2\ 2p^2\ 2p^1\ 2p^1$). Since O-atom is highly electronegative, it can accept two electrons to form oxide ion (O^{2-}) which has noble gas stable configuration. Thus O-atom generally shows –2 oxidation state. On the other hand, since other elements like sulphur ($S = 3s^2\ 3p^2\ 3p^1\ 3p^1\ 3d^\circ\ 3d^\circ$.....) have empty 3*d*-orbitals in their valence-shell, an electron from the completely-filled 3*p* orbital and one electron from the completely-filled 3*s* orbital to the empty 3*d* orbitals can be promoted to get 4 and 6 unpaired electrons. The presence of 2 [S = $3s^2\ 3p^2\ 3p^1\ 3p^1\ 3d^\circ\ 3d^\circ$ (n = 2)], 4 [S* = $3s^2\ 3p^1\ 3p^1\ 3p^1\ 3d^1\ 3d^\circ$ (n = 4)] and 6 [S** = $3s^1\ 3p^1\ 3p^1\ 3p^1\ 3d^1\ 3d^1$($n$ = 6)] unpaired electrons in S-atom explains its +2, +4 and +6 oxidation states.

(*vii*) Oxygen cannot show oxidation states of +4 and +6 but sulphur atom can do so.

Ans : Since O-atom (O = $2s^2\ 2p^2\ 2p^1\ 2p^1$) does not have *d*-orbitals in its valence shell, the promotion of an electron from the completely-fillled 2*p* or 2*s* orbitals is not possible and hence 4 or 6 unpaired electrons cannot be obtained. Thus O-atom cannot show oxdation states of +4 and +6. On the other hand, in S-atom (S = $3s^2\ 3p^2\ 3p^1\ 3p^1\ 3d^\circ\ 3d^\circ$...), one electron from 3*p* orbital can be promoted to the empty 3*d* orbital to get 4 unpaired electrons. Similarly the promotion of an electron from 3*s* orbital to the empty 3*d* orbital can be done to get 6 unpaired electrons. Thus S-atom can show +4 and +6 oxidation states due to the presence of 4 and 6 unpaired electrons respectively.

(*viii*) Negative electron gain enthalpy of O-atom is lower than that of S-atom (O = –141 KJmol^{-1}, S = – 200KJmol^{-1}).

Ans : Since 2*p* orbitals in O-atom are relatively smaller in szie than 3*p* orbitals in S-atom, electron-electron repulsions are comparatively larger in O-atom. Hence O-atom cannot accept the incoming electron so easily as S-atom can do. Consequently energy released in the formation of $O^-(g)$ from $O(g)$ is less than that released in the formation of $S^-(g)$ from $S(g)$. In other words *negative electron gain enthalpy of O-atom is less than that of S-atom.*

$$O(g) + e^- \rightarrow O^-(g),\ \Delta H = -\Delta eg = -141 \text{ KJmol}^{-1}$$

$$S(g) + e^- \rightarrow S^-(g),\ \Delta H = -\Delta eg = -200\text{KJmol}^{-1}$$

(*ix*) The compounds of fluorine with oxygen are called fluorides of oxygen and not oxides of fluorine.

Ans : Since F-atom has higher electronegativity than O-atom, compounds of F with O are called fluorides of oxygen and not oxides of fluorine. For example F_2O is called *oxygen difluoride* and not *difluorine oxide*. This compound is, therefore, represented as OF_2 and not F_2O.

(*x*) Elements of group 16 generally show lower value of first ionization enthaply compared to the corresponding elements of group 15.

Ans : This is because of the following two reasons :

(*i*) Due to extra stability of the exactly half-fillled *p*-orbitals electronic configuration of group 15 elements, they require larger amount of energy to remove an electron as compared to those of group 16 elements.

(*ii*) After removal of an electron, the group 16 elements yield species which have more stable exactly half-filled *p*-orbitals electronic configuration while this is not so in case of group 15 elements.

Q.3 Name the element of group 16 which has : (*i*) highest electronegativity (*ii*) highest metallic character (*iii*) highest melting point. (*iv*) Maximum ionisation energy (*v*) Maximum catenation property.

Ans : (*i*) *Oxygen has the highest electronegativity.*

Explanation. Since the atomic size of the elements increases down the group, the electronegativity values of the elements decrease down the group. Thus oxygen has the highest electronegativity.

(*ii*) *Polonium has the highest metallic character.*

Explanation. Due to the decrease in IE values down the group, metallic character of the elements increases. Thus Po has the highest metallic character.

(*iii*) *Tellurium has the highest melting point.*

Explanation. Since the van der Waal's forces of attraction between the atoms of elements increases down the group, the melting points of the elements also increase down the group from O to Te. Po has lower m.pt. than Te. Thus the actual order of m.pts. is O < S < Se < Te > Po.

(*iv*) *Oxygen has the highest ionisation energy.*

Explanation. Due to the increase in the size of the atoms of the elements on moving down the group from O to Po, ionisation energies of the elements decrease down the group. Thus oxygen has the highest ionisation energy.

(*v*) *Sulphur has the maximum catenation property.*

Explanation. Catenation property of an element (M) increases with the increase of the strength of M–M bond. Since among the elements of group 16, S–S bonds are the strongest, sulpher has the maximum catenation property.

Q.4 Explain the following :

(*i*) The two sulphur-oxygen bonds in SO_2 molecule are equal (= 143 pm).

Ans : In SO_2, S is sp^2 hybridized. Two of the three sp^2 orbitals form two bonds while the third contains the lone pair of electrons. S is now left with one half-fillled *p*-orbital and one half-filled *d*-orbital. These form one $p\pi - p\pi$ and $d\pi - p\pi$ double bond with oxygen atom. Thus, SO_2 has bent structure with OSO bond angle of 119.5. Due to resonance, the two π-bonds are equal (143 pm).

(*ii*) SO_2 is a more powerful reducing agent (RA) in alkaline medium than in acidic medium. (I.I.T.1992)

Ans : In presence of moisture, SO_2 can produce nescent hydrogen and hence acts as a reducing agent. When SO_2 reduces a certain susbtance, it gets oxidised to SO_3 which is further oxidised to H_2SO_4.

$$\begin{array}{l} SO_2 + H_2O \rightleftharpoons SO_3 + 2H \\ SO_3 + H_2O \rightleftharpoons H_2SO_4 \\ \hline SO_2 + 2H_2O \rightleftharpoons H_2SO_4 + 2H \end{array}$$

This equation shows that when SO_2 acts as a reducing agent, it gets oxidised to H_2SO_4. In presence of an alkali, H_2SO_4 formed as above reacts with the alkali and gets neutralised by it. Thus the equlibrium of the above reaction is shifed towards right and hence more quantity of nescent hydrogen is produced. Thus in presence of alkali, SO_2 acts as a stronger R.A. In presence of an acid, the equilibrium gets shifted towards left and hence lesser quantity of nescent hydrogen is formed. This makes SO_2 to act as a weaker R.A. Thus in presence of an acid SO_2 acts as a weaker R.A.

Oxidation of SO_2 to H_2SO_4 in acidic and basic medium can be shown as :

$$\left.\begin{array}{ll} & SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H \\ \text{or} & SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^- \end{array}\right\} \textit{In acidic medium}$$

$$\left.\begin{array}{ll} & SO_2 + 2NaOH + \frac{1}{2}O_2 \longrightarrow Na_2SO_4 + H_2O \\ \text{or} & SO_2 + 4OH^- + \longrightarrow SO_4^{2-} + 2H_2O + 2e^- \end{array}\right\} \textit{In basic medium}$$

***(iii)* All the three sulphur-oxygen bonds in SO_3 molecule are identical.**

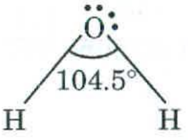
Ans : The equivalence of all the three sulphur-oxygen bonds in SO_3 molecule suggests that the actual structure of SO_3 molecule is a resonance hybrid of the three structures.

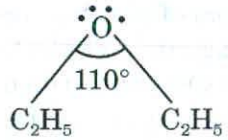
Q.5 Find out the oxidation state of S-atom in SF_6 and SH_6 molecules.

Ans : Electronegativity values of S, F and H are S = 2.44, F = 4.00 and H = 2.20. Since S-atom has lower electronegativity than F-atom, in SF_6 molecule S-atom shows positive oxidation state (= +6) and F-atom shows negative oxidation state (= –1). On the other hand, since S-atom has higher electronegativity than H-atom, in SH_6 molecule S-atom shows negative oxidation state (= –6) and H-atom has positive oxidation state (= +1). Thus oxidation state of S-atom in SF_6 = +6 and oxidation state of S-atom in SH_6 = –6.

Q.6 Although the central O-atom in water (H_2O) and diethylether, $(C_2H_5)_2O$ has the same hybridisation, get these molecules have different bond angles. (H_2O = 104.5°, $(C_2H_5)_2O$ = 110°). Expalin.

Ans : The central O-atom in H_2O and $(C_2H_5)_2O$ both is sp^3 hybridised. Hence both molecules are expected to have the same bond angles. In $(C_2H_5)_2O$ molecule, the repulsion between two bonding electron pairs (*i.e.* electron pairs involved in two $O - C_2H_5$ bonds) is greater than that between two bonding electron pairs in H_2O molecule (*i.e.* electron pairs involved in two O – H bonds). Hence $C_2H_5 - O - C_2H_5$ bond angle in $(C_2H_5)_2O$ is greater (= 110°) than H – O – H bond angle in H_2O (= 104.5°).





Q.7 Among the hydrides of group 16, water shows unusual physical properties. Why ? ***(D.B.S 2003)***

Ans : Due to high eiectronegativity of O, the O–H bond in H_2O froms strong intermolecular H-bonds. As a result, water exists as an associated molecule while other hydrides of group 16 do not form H-bonds and hence exist as discrete molecules. As a result, water shows unusual physical properties, *i.e.* high b.p., high thermal stability and weaker acidic character as compared to other hydrides of group 16.

Q.8 Why H_2O is a liquid while H_2S is a gas ? ***(H.S.B 2001)***

Ans : There is H-bonding in H_2O due to high electronegativity and small size of O-atom but there is no H-bonding in H_2S.

Q.9 H_2S is acidic while H_2O is neutral. Explain.

Ans : The S–H bond is weaker than O–H bond because size of S-atom is bigger than that of O-atom. Hence, H_2S can dissociate to give H^+ ions in aqueous solution.

Q.10 Among the hydrides of group 16 elements :

(*i*) Which has the lowest boling point.

Ans : *H_2S has the lowest boiling point. ($H_2O > H_2Te > H_2Se > H_2S$)*

Explanation. Due to the increase in van der Waals forces of attraction from H_2S to H_2Te, the boiling points of these hydrides also increase from H_2S to H_2Te ($H_2S < H_2Se < H_2Te$). However, the boiling point of H_2O is the highest. Thus the overall order of boiling points is $H_2S < H_2Se < H_2Te < H_2O$. This order shows that H_2S has the lowest boiling point.

(*ii*) Which has the maximum thermal stability.

Ans : *H_2O has the maximum thermal stability ($H_2O > H_2S > H_2Se > H_2Te$)*

Expalnation. Due to the increase in the size of M-atom from O to Te in H_2M molecules (M = O, S, Se, Te), M – H bond becomes weaker and weaker on moving down the group from H_2O to H_2Te and hence thermal stability of H_2M molecules decreases from H_2O to H_2Te ($H_2O > H_2S > H_2Se > H_2Te$). Obiviously H_2O has the maximum thermal stability.

(*iii*) Which has the weakest acidic character.

Ans : *H_2O has the weakest acidic character. In fact H_2O is neutral [H_2O (neutral) $< H_2S < H_2Se < H_2Te$)].*

Explanation. The acidic character of H_2M molecules (M = O, S, Se, Te) increases from H_2O to H_2Te. Due to the increase in the size of M-atom from O to Te, M – H bond distance in H_2M molecules also increases from O – H to Te – H. Because of the increase in M–H bond distance, this bond becomes weaker and weaker and hence the cleavage of this bond to produce H as proton (H^+) becomes easier and easier. Thus the tendency of H_2M molecules to give H^+ (or the acidic character or acidic strength of H_2M molecules) increases from H_2O to H_2Te. Thus H_2O has the minimum acidic character. In fact H_2O does not show acidic character. It is a neutral hydride.

(*iv*) Which is liquid at room temperature.

Ans : *Water (H_2O) is liquid at room temperature. Other hydrides are gases*

Explanation. Due to the highest EN of O-atom, H_2O molecule undergoes intermolecular H-bonding and forms associated molecule, $(H_2O)_n$. Since in order to break H-bonds present in $(H_2O)_n$ a large amount of heat energy is required, H_2O exists as a liquid at room temperature.

(*v*) Which has the highest bond angle.

Ans : *H_2O has the highest bond angle.*

Explanation. The highest value of bond angle in H_2O is due to the fact that the distance between the two adjacent bps in H_2O molecule is minimum. Hence repulsion between these bps is maximum (strongest) and HOH bond angle is also maximum.

Q.11 Arrange the oxoacids of S, Se and Te given in the following sets in the decreasing order of their acid strength: (*a*) H_2SO_3, H_2SeO_3 and H_2TeO_3 (*b*) H_2SO_4, H_2SeO_4 and H_2TeO_4.

Ans : The acid strength of oxoacids of S, Se and Te with the same oxidation state decreases in moving down the group from S to Te. Thus :

(*a*) $\overset{+4}{H_2SO_3} > \overset{+4}{H_2SeO_3} > \overset{+4}{H_2TeO_3}$ (O.S. of element = +4)

(*b*) $\overset{+6}{H_2SO_4} > \overset{+6}{H_2SeO_4} > \overset{+6}{H_2TeO_4}$ (O.S. of element = +6)

Q.12 Arrange the oxyacids given the following sets in the increasing order of their acid strength : (*a*) H_2SO_3 and H_2SO_4 (*b*) H_2SeO_3 and H_2SeO_4 (*c*) H_2TeO_3 and H_2TeO_4.

Ans : Acid strength of oxoacids of an element of group VI A in different oxidation states increases with the increase in oxidation state of the element. Thus :

(*a*) $\overset{+4}{H_2SO_3} < \overset{+6}{H_2SO_4}$

(*b*) $\overset{+4}{H_2SeO_3} < \overset{+6}{H_2SeO_4}$

(*c*) $\overset{+4}{H_2TeO_3} < \overset{+6}{H_2TeO_4}$

University Questions

1. Discuss the position of sixth group elements namely O, S, Se and Te in the periodic table. (*Jiwaji 84*)
2. Discuss the anomalous behaviour of oxygen in it group. (*Agra 84*)
3. Explain the following, giving appropriate reasons :
    (1) The bond lengths of covalent bonds in SO_2 and SeO_2 molecules are much shorter than expected. (*Delhi 87*)
    (2) Sulphur does not form S_2 molecule like O_2 molecule given by oxygen. (*Raj. 86 S*)
    (3) OF_6 does not exist while SF_6 exists. (*Punjab; Raj. 86*)
    (4) SF_6 is chemically inert. (*Poona 86*)
    (5) The formula of telluric acid is H_6TeO_6 or $Te(OH)_6$. The analogous sulphuric acid H_6SO_6 or $S(OH)_6$ is not known.
    or Tellurium forms H_6TeO_6 but sulphur does not form H_6SO_6. (*Delhi Hons. 87*)

(6) SF_6 is chemically inert whereas SF_4 is hydrolysed even though the average bond energy is SF_4 is greater than that in SF_6. *(Delhi Hons. 87)*

(7) Oxygen forms only a difluoride, while sulphur forms a hexafluoride. *(Allahabad 89)*

(8) Although the central atom in the hexafluorides SF_6, SeF_6 and TeF_6 belongs to the same group, it is only TeF_6 which can be hydrolysed by H_2O. SF_6 and SeF_6 both remain unreactive. *(Allahabad 87)*

(9) Oxygen molecule is O_2 but sulphur molecule is S_8. *(Madurai 86; M.D. Rohtak 83)*

(10) Unlike SO_2, SeO_2 is a solid that has a chain structure. *(Delhi Hons. 87)*

(11) Oxygen is a gas while sulphur and selenium are solids. *(Madras 86)*

(12) The strength of hydroxides of elements of oxygen family increases with increase in atomic number of element. *(Poona 86)*

(13) SF_6 ii known but SCl_6 is not known. *(Delhi 85)*

(14) Hydride of oxygen is less acidic than the hydride of tellurium. *(GND 82)*

(15) The hydride of oxygen is a liquid of high b. pts. While that of sulphur is a gas at room temperature. *(Punjab 85; Madras 86; Raj. 86 S; Delhi 81, 87, 88; Bundelkhand 88; Madurai 84; MLNR 82; Allahabad 87, 89; Calcutta 81; Meerut 84 S)*

(16) H_2O has higher b.pt than H_2S. *(Madras 85; Delhi 81; Raj. 83)*

(17) The boiling point of H_2O is much higher than the values of the outer hydrides of VI group. *(Bharathidasan 85; Andhra 86)*

(18) H_2S more polar than H_2O. *(M.D. Rohtak 84)*

(19) H_2S is a better reducing agent than H_2O.

(20) H_2S less, stable than H_2O.

(21) The bond angles of the hydrides of oxygen family decrease with the increase in atomic number of element.

or Bond angles decrease from H_2O, H_2S, H_2Se, to H_2Te. *(GND 85, 86)*

or Bond angles in H_2O, H_2S, and H_2Se are 104.5°, 92.2° and 91.0° respectively. *(Punjab 84)*