विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचितः मानव धर्म प्रणेता
सद्गुरु श्री रणछोड़दासजी महाराज

STUDY PACKAGE

This is TYPE 1 Package please wait for Type 2

Subject : CHEMISTRY

Topic : NITROGEN FAMILY

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NITROGEN FAMILY

Nitrogen(N_2)

Occurence: Nitrogen is widely distributed in nature both in free as well as in the combined state. Air is the most abundant source of free nitrogen. It forms 75% by mass and 78% by volume of the air. In combined state, it is found as nitrates such as Chile saltpetre ($NaNO_3$), Indian saltpetre (KNO_3) and ammonium comopunds.

Preparation: Nitrogen can be obtained from the following two sources:
(i) Nitrogen Compounds (ii) Air

(i) Nitrogen from nitrogen compounds: (a) Nitrogen in the laboratory can be obtained by heating ammonium nitrite or ammonium dichromate.

$$NH_4Cl + NaNO_2 \longrightarrow \underset{\text{Ammonium nitrite}}{NH_4NO_2} + NaCl$$

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

Nitrogen is collected by downward dispalcement of water.

(b) Pure nitrogen can be obtained by passing the ammonia vapours over heated CuO.

$$2NH_3 + 3CuO \longrightarrow N_2 + 3Cu + 3H_2O$$

NH_3 can also be oxidised to nitrogen by Cl_2, Br_2, a hypochlorite, a hypobromite or bleaching powder.

(c) It can be obtained by the action of nitrous acid (or $NaNO_2$ and dil. H_2SO_4) on urea.

$$\underset{\text{Urea}}{NH_2CONH_2} + 2HNO_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$

(d) Pure nitrogen is obtained in small amounts by heating sodium or barium azides in vacuum.

$$\underset{\text{Barium azide}}{Ba(N_3)_2} \longrightarrow 3N_2 + Ba$$

(ii) From air: (a) Commercially nitrogen is obtained by liquefaction of air. The resultant liquid isfractionally distilled in *Claude's apparatus*.

(b) By removing oxygen of the air with the use of chemical substances.

$$\text{Purified air} \longrightarrow \text{Hot Cu} \longrightarrow \text{Nitrogen}$$

$$2Cu + O_2 \longrightarrow 2CuO$$

$$\text{Purified air} \longrightarrow \text{Hot Cake} \longrightarrow CO_2, CO, N_2$$

CO_2 and CO are removed by usual methods.

$$\text{Purified air} \longrightarrow \text{Phosphorus} \longrightarrow P_2O_5 + N_2$$

$$P_2O_5 \xrightarrow{H_2O} H_3PO_4$$

Properties:

(i) It is a colourless, tasteless and odourless gas. It is slightly lighter than air as its vapour density is 14.0. It is sparingly soluble in water.

(ii) It can be liquefied to a colourless liquid (b. pt. –195.8^{0}C).

(iii) It does not help in combustion. Nitrogen itself is non-combustible.

(iv) It is chemically inert under ordinary conditions. However, it shows chemical activity under high temperatures.

(a) Nitrogen combines with oxygen under the influence of very high temperature like electric spark.

$$N_2 + O_2 \xrightleftharpoons{3000^\circ C} 2NO \text{ (Nitric oxide)}$$

(b) Nitrogen combines with hydrogen in the presence of a catalyst (finely divided iron) at 200 atmospheres and 400-500^{0}C temperature.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \text{ (Ammonia)}$$

(c) Nitrogen combines with metals at red heat to form nitrides.

$$6Li + N_2 \xrightarrow{450^0C} 2Li_3N \text{ (Lithium nitride)}$$

$$3Mg + N_2 \xrightarrow{450^0C} Mg_3N_2 \text{ (Magnesium nitride)}$$

$$2Al + N_2 \xrightarrow{800^0C} 2AIN \text{ (Aluminium nitride)}$$

Non-metals like boron, silicon at bright red heat also combine with nitrogen.

$$2B + N_2 \longrightarrow 2BN \text{ (Boron nitride)}$$

$$3Si + 2N_2 \longrightarrow Si_3N_4 \text{ (Silicon nitride)}$$

(d) Nitrogen combines with calcium carbide to form calcium cyanamide at 1000^{0}C.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

The mixture of calcium cyanamide and carbon is technically known as nitrolinm.

Uses: It is used in the manufacture of NH_3, HNO_3, $CaCN_2$ and other nitrogen compounds.

Active nitrogen: When an electric discharge is allowed to pass through nitrogen under very low pressure (about 2 mm), a brialliant luminiscence is observed which persists for sometime after the stoppage of the discharge. It is observed that nitrogen after the discharge is more active. This nitrogen is termed **active nitrogen.**

The exact nature of active nitrogen is not yet known.

Important compounds of Nitrogen

1. Ammonia

Nitrogen forms three well known hydrides with hydrogen:
(i) Ammonia, NH_3, (ii) Hydrazine, $NH_2 \cdot NH_2$ (N_2H_4); (iii) Hydrazoic acid, N_3H. Ammonia is the most important of these hydrides.

Occurence: NH_3 is found in traces in atmopshere. Ammonium salts such as ammonium chloride and ammonium sulphate are found in small amounts in the soil.

Discovery: It was first isolated by Priestly by the action of ammonium chloride and lime. It was named alkaline air.

Preparation: (i) Ammonium is obtained on a small scale from ammonium salts which evolve it when heated with caustic soda or lime.

$$NH_4Cl + NaOH \longrightarrow NH_3 + NaCl + H_2O$$

(Laboratory Preparation) $2NH_4Cl + \underset{\text{(slaked lime)}}{Ca(OH)_2} \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$

(ii) Ammonia is formed when ammonium chloride is heated with litharge.

$$2NH_4Cl + PbO \longrightarrow 2NH_3 + PbCl_2 + H_2O$$

(iii) By reacting nitrides with water, ammonia is obtained.

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

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

(iv) Ammonium can also be formed by doing reduction of nitrates and nitrites with zinc and caustic soda. Zinc and caustic soda produce nascent hydrogen which reacts with nitrates and nitrites to form ammonia.

$$NaNO_3 + 8H \xrightarrow{Zn/NaOH} NaOH + NH_3 + 2H_2O$$

$$NaNO_2 + 6H \xrightarrow{Zn/NaOH} NaOH + NH_3 + H_2O$$

(v) Calcium cyanamide is also obtained by heating ammonium compounds.

$$\underset{\substack{\text{Ammonium}\\\text{sulphate}}}{(NH_4)_2SO_4} \xrightarrow{\text{Heat}} NH_3 + \underset{\substack{\text{Ammnoium hydrogen}\\\text{sulphate}}}{NH_4HSO_4}$$

$$\underset{\substack{\text{Ammonium}\\\text{dihydrogen phosphate}}}{NH_4H_2\cdot PO_4} \xrightarrow{\text{Heat}} NH_3 + \underset{\substack{\text{Metaphosphoric}\\\text{acid}}}{HPO_3} + H_2O$$

(vi) Urea on treatment with caustic soda forms ammonia.

$$\underset{\text{urea}}{NH_2CONH_2} + 2NaOH \longrightarrow Na_2CO_3 + 2NH_3$$

Drying of Ammonia gas:

The common dehydrating agents like sulphuric acid or $CaCl_2$ or P_2O_5 cannot be used as these react with ammonia.

$$2NH_3 + H_2SO_4 \longrightarrow \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4}$$

$$CaCl_2 + 8NH_3 \longrightarrow \underset{\text{Addition product}}{CaCl_2\cdot 8NH_3}$$

$$P_2O_5 + 6NH_3 + 3H_2O \longrightarrow \underset{\text{Ammonium phosphate}}{2(NH_4)_3PO_4}$$

Fro drying, quick lime is used as it does not react with ammonia but reacts readily with moisture.

$$\underset{\text{quick lime}}{CaO} + H_2O \longrightarrow Ca(OH)_2$$

Manufacture of Ammonia:

(i) Haber's process: The method involves the direct combination of nitrogen and hydrogen according to the following reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 24.0 \text{ kcal}$$

Raw materials: Nitrogen and hydrogen are the chief raw materials. Nitrogen is obtained from air by liquefaction followed by fractional evaporation of liquid air. Hydrogen is obtained by electrolysis of water.

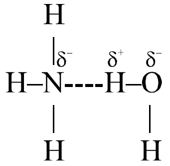
(ii) Bosch Process: From Powder gas & water gas

(iii) Cyanamide process: $CaCN_2 + \underset{\text{(steam)}}{3H_2O} \xrightarrow[\text{3-4 atm}]{180^0C} CaCO_3 + 2NH_3$

(iv) From ammoniacal liquor obtained during coal distillation: Large quantities of ammonia are obtained as a by-product in the manufacture of coal gas.

Physical properties: (i) Ammonia is a colourless gas with a characterstic pungent odour. it brings tears into the eyes.

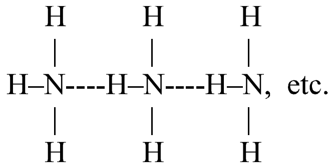
(ii) It is highly soluble in water. This high solubility is due to the hydrogen bonding. The solubility of ammonia increases with increase of pressure and decreases with increase of temperature.



$$\begin{array}{c} H \\ | \\ H\!-\!\overset{\delta^-}{N}\text{----}\overset{\delta^+}{H}\!-\!\overset{\delta^-}{O} \\ |\qquad\quad | \\ H\qquad\quad H \end{array}$$

(iii) It can be easily liquefied at room temperature by the application of pressure.

(iv) Ammonia molecules link together to form associated molecules through hydrogen bonding.



$$H_2N\text{–}H\text{----}H_2N\text{–}H\text{----}H\text{–}NH_2,\ \text{etc.}$$

Higher melting point and boiling point in comparison to other hydrides of V group are due to hydrogen bonding.

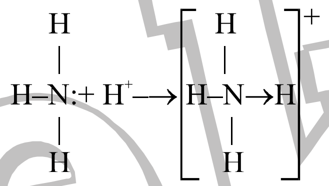
Chemical Properties:(i) Stability : It is highly stable. It decomposes into nitrogen and hydrogen at red heat or when electric sparks are passed through it.

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

(ii) Combustion: Ordinary, ammonia is neither combustible nor a supporter of combustion. However, it burns in the presence of oxygen to form nitrogen and water.

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

(iii) Basic nature: Ammonia is a Lewis base, accepting proton to form ammonium ion as it has tendency to donate an electron pair.



$$H_3N: + H^+ \longrightarrow [H_3N\rightarrow H]^+$$

It forms salts with acids.

$$NH_3 + HCl \longrightarrow \underset{\text{Thick white fumes}}{NH_4Cl} \qquad \text{(Ammonium chloride)}$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \qquad \text{(Ammonium sulphate)}$$

It's solution is a weak base. the solution is described as aqueous ammonia. It's ionisation in water is represented as:

$$NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

The solution turns red litmus to blue and phenolphthalein pink.

(iv) Oxidation: It is oxidised to nitrogen when passed over heated CuO or PbO

$$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$$

$$3PbO + 2NH_3 \longrightarrow 3Pb + N_2 + 3H_2O$$

Both chlorine and bromine oxidise ammonia.

$$2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$$

$$6NH_3 + 6HCl \longrightarrow 6NH_4Cl$$

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

When chlorine is in excess an explosive substance nitrogen trichloride is formed.

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

Iodine flakes when rubbed with liquor ammonia form a dark brown precipitate of ammoniated nitrogen iodide which explodes readily on drying.

$$2NH_3 + 3I_2 \longrightarrow NH_3\cdot NI_3 + 3HI$$

Hypochlorites and hypobromites oxidise ammonia to nitrogen.

$$2NH_3 + 3NaClO \longrightarrow N_2 + 3NaCl + 3_2O$$

The oxidation of ammonia with bleaching powder occurs on warming.

$$3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + N_2 + 3H_2O$$

Thus, ammonia acts as a reducing agent.

The restricted oxidation of NH_3 can be done with air, when the mixture is passed over heated platinum gauze at 700-800^{0}C.

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

This is the Ostwald's process and used for the manufacture of HNO_3.

(v) Formation of amides: When dry ammonia is passed over heated sodium or potassium, amides are formed with evolution of hydrogen.

$$2Na + 2NH_3 \longrightarrow \underset{\text{Sodamide}}{2NaNH_2} + H_2$$

(vi) Reactions of aqueous ammonia: Many metal hydroxides are formed which may be precipitated or remain dissolved in the form of complex compound in excess of NH_4OH.

$$FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{ppt.}}{Fe(OH)_3} + 3NH_4Cl$$

$$AlCl_3 + 3NH_4OH \longrightarrow \underset{\text{ppt.}}{Al(OH)_3} + 3NH_4Cl$$

$$CrCl_3 + 3NH_4OH \longrightarrow \underset{\text{ppt.}}{Cr(OH)_3} + 3NH_4Cl$$

$$CuSO_4 + 2NH_4OH \longrightarrow \underset{\text{Blue ppt.}}{Cu(OH)_2} + (NH_4)_2SO_4$$

$$Cu(OH)_2 + (NH_4)_2CO_4 + 2NH_4OH \longrightarrow \underset{\substack{\text{Tetramine copper}\\ \text{sulphate}\\ \text{(colourless solution)}}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

$$CdSO_4 + 4NH_4OH \longrightarrow \underset{\substack{\text{Cadmium tetramine}\\ \text{sulphate}\\ \text{(Colourless solution)}}}{[Cd(NH_3)_4]SO_4} + 4H_2O$$

$$AgNO_3 + NH_4OH \longrightarrow \underset{\text{White ppt.}}{AgOH} + NH_4NO_3$$

$$AgOH + 2NH_4OH \longrightarrow \underset{\text{soluble}}{[Ag(NH_3)_2](OH)} + 2H_2O$$

AgCl also dissolve in NH_4OH solution

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Diamine silver chloride}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

$$ZnSO_4 + 2NH_4OH \longrightarrow \underset{\text{ppt.}}{Zn(OH)_2} + (NH_4)_2SO_4$$

$$Zn(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \longrightarrow \underset{\substack{\text{Tetramine zinc sulphate}\\ \text{(soluble) colourless}}}{[Zn(NH_3)_4]SO_4} + 4H_2O$$

Nickel salt first gives a green precipitate which dissolves in excess of NH_4OH.

$$NiCl_2 + 2NH_4OH \longrightarrow Ni(OH)_2 + 2NH_4Cl$$

$$Ni(OH)_2 + 2NH_4Cl + 4NH_4OH \longrightarrow [Ni(NH_3)_6]Cl_2 + 6H_2O$$

It forms a white precipitate with mercuric chloride.

$$HgCl_2 + 2NH_4OH \longrightarrow \underset{\substack{\text{Amido mercuric}\\ \text{chloride}}}{HgNH_2Cl} + NH_4Cl + H_2O$$

It forms a grey precipitate with mercurous chloride.

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{Hg + HgNH_2Cl}_{\text{Grey}} + NH_4Cl + H_2O$$

(vii) Reaction with Nessler's reagent: A reddish brown ppt. is formed.

$$2KI + HgCl_2 \longrightarrow HgI_2 + 2KCl$$
$$2KI + HgI_2 \longrightarrow K_2HgI_4$$

Alkaline solution of K_2HgI_{44} is called Nessler's reagent.
This gives brown ppt. with NH_3 called iodide of Million's base.

$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow \underset{\text{Brown ppt.}}{H_2NHgOHgI} + 7KI + 2H_2O$$

Uses: (i) Liquid hydrogen is not safe to transport in cylinders. Ammonia can be easily liquefied and transported safely in cylinders. Ammonia can be decomposed into hydrogen and nitrogen by passing over heated metallic catalyst. Thus, ammonia is the source for the production of hydrogen at any destination.
(ii) Ammonia is also used in the manufacture of urea which is an excellent fertilizer of nitrogen.

Hydrazine or Diamide NH_2NH_2 or N_2H_4

This is another hydride of nitrogen. It is prepared by following methods:

(i) Raschig's method: A strogn aqueous solution of ammonia is boiled with sodium hypochlorite in presence of a little glue.

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$
$$\underset{\text{Chloramine}}{NH_2Cl} + NH_3 \longrightarrow \underset{\text{Hydrazine}}{NH_2 \cdot NH_2} + HCl$$

$$2NH_3 + NaOCl \longrightarrow NH_2NH_2 + NaCl + H_2O$$

It burns in air liberating huge amount of energy. The alkyl derivatives of hydrazine are used these days as potential rocket fuels. It reacts with nitrous acid to give hydrazoic acid, N_3H.

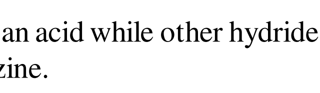
$$N_2H_4 + HNO_2 \longrightarrow N_3H + 2H_2O$$

Hydrazine and its salts act as powerful reducing agents.

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

It reduces Fehling's solution to red cuprous oxide, iodates to iodides and decolourises acidified $KMnO_4$ solution. It is used as a fuel for rockets, reducing agent and a reagent in organic chemistry.

Structure



Hydrazoic Acid, N_3H

It is the third hydride of nitrogen. It is an acid while other hydrides, NH_3 and N_2H_4 are bases. It is prepared by the action of nitrous acid on hydrazine.

$$NH_2 \cdot NH_2 + HNO_2 \longrightarrow N_3H + 2H_2O$$

It is also formed in the form of sodium salt by passing nitrous oxide on sodamide.

$$\begin{tikzcd} \underset{\text{Sodium}}{Na} \arrow[r, "\text{Dry } NH_3"] & \underset{\text{Sodamide}}{NaNH_2} \arrow[r, "N_2O"] & \underset{\text{Sodium azide}}{NaN_3} \arrow[d, "H_2SO_4"] & + \quad H_2O \\ & & N_3H & \end{tikzcd}$$

It reduces acidified $KMnO_4$, nitrous acid, etc.

$$2N_3H + O \longrightarrow 3N_2 + H_2O$$

$$N_3H + HNO_2 \longrightarrow N_2 + N_2O + H_2O$$

It oxidises HCl into Cl_2

$$N_3H + 2HCl \longrightarrow N_2 + NH_3 + Cl_2$$

Oxides of Nitrogen

N_2O_3 and N_2O_5 monomeric other are dimeric

Nitrogen forms a number of oxides. The well known oxides of nitrogen are:

(i) Nitrogen oxide, N_2O
(ii) Nitric oxide, NO
(iii) Nitrogen trioxide, N_2O_3
(iv) Nitrogen dioxide or Di-nitrogen tetroxide, NO_2 or N_2O
(v) Nitrogen pentoxide, N_2O_5

(I) Nitrogen Oxide, N_2O or Laughing Gas (Neutral)

Preparation:

It can be prepared by heating ammonium nitrate or a mixture of sodium nitrate and ammonium sulphate.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

$$2NaNO_3 + (NH_4)_2SO_4 \rightarrow 2NH_4NO_3 + Na_2SO_4$$

$$\downarrow$$

$$2N_2O + 4H_2O$$

$$FeSO_4 + NO \rightarrow \underset{\text{Addition product}}{FeSO_4.NO}$$

$$H_2SO_4 + 2NH_3 \rightarrow \underset{\text{Ammonium Sulphate}}{(NH_4)_2SO_4}$$

The following reactions can also be used to prepare nitrous oxide.

$$NaNH_2 + N_2O \rightarrow NaN_3 + NaOH + NH_3$$

(a) By the action of cold and dilute nitric acid on zinc metal.

$$Fe/4Zn + 10HNO_3 \rightarrow 4Zn\,(NO_3)_2 + N_2O + 5H_2O$$

(b) By reducing nitric acid with stannous chloride and hydrochloric acid.

$$4SnCl_2 + 8HCl + 2HNO_3 \rightarrow 4SnCl_4 + N_2O + 5H_2O$$

(c) By reducing nitric oxide with sulphur dioxide.

$$2NO + SO_2 + H_2O \rightarrow H_2SO_4 + N_2O$$

(d) By heating the mixture of hydroxylamine hydrochloride and sodium nitrite (1 : 1)

$$NH_2OH.HCl + NaNO_2 \rightarrow N_2O + NaCl + 2H_2O$$

Properties:

(a) It is a colourless gas with pleasant odour and sweet taste.

(b) When inhaled in moderate quantity, it produces hysterical laughter, hence named as laughing gas. However, when inhaled for long, it produces insensibility and may prove fatal too.

(c) It is heavier than air.

(d) It is fairly soluble in cold water but not in hot water.

(e) It is neutral to litmus.

(f) It does not burn but support combustion. The burning material decompose nitrous oxide into nitrogen and oxygen. The oxygen then helps in the buring.

$$2N_2O \xrightarrow{520-900^\circ C} 2N_2 + O_2$$

It supports combustion of sulphur, phosphorus, magnesium, sodium, candle and a splineter.

$$S + 2N_2O \rightarrow SO_2 + 2N_2$$
$$4P + 10N_2O \rightarrow 2P_2O_5 + 10N_2$$
$$Mg + N_2O \rightarrow MgO + N_2$$

(g) It is decomposed by red hot copper.

$$Cu + N_2O \rightarrow CuO + N_2$$

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

$$N_2O + H_2 \rightarrow N_2 + H_2O$$

(i) $N_2O + NaNH_2 \rightarrow NaH_3 + NH_3 + NaOH$

Uses:

(i) It is used as the propellant gas for whipped ice-cream.

(ii)A mixture of nitrous oxide and oxygen is used as an ananesthetic in dental and other minor surgical operations.

Structure:

N_2O is linear and unsymmetrical molecule. It is considered as a resonance hybrid of the following two structures:

$$:\ddot{N}\underset{\pi}{\overset{\sigma}{=}}\overset{+}{N}\underset{\pi}{\overset{\sigma}{=}}\ddot{O}: \leftrightarrow :N\underset{2\pi}{\overset{\sigma}{=}}\overset{+}{N}\overset{\sigma}{-}\overset{-}{\underset{..}{\ddot{O}}}:$$

It has a very small value of dipole moment (0.116D)

Tests:

(i) It has sweet smell.

(ii) It supports the combustion of glowing splinter.

(iii) It does not form brown fumes with nitric oxide.

(iv) N_2O does not form $H_2N_2O_2$ with H_2O nor hyponitrites with alkali.

(II) Nitric oxide, NO Neutral

Preparation:

(a) By the action of dilute nitric acid on copper (Lab. Method). the nitric oxide liberated is collected over water.

$$Ag/Hg/Pb/3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

The liberated gas may contain NO_2 and N_2O. These are separated by passing the mixture through ferrous sulphate solution. NO forms a dark nitroso-ferrous sulphate. When this solution is heated, pure nitric oxide is liberated.

$$\underset{\text{(impure gas)}}{FeSO_4 + NO} \rightarrow \underset{\text{(Dark Brown)}}{FeSO_4.NO} \xrightarrow{\text{heate}} \underset{\text{(Pure gas)}}{FeSO_4 + NO}$$

(b) A pure sample of nitric oxide is obtained when a mixture of KNO_3, $FeSO_4$ and dilute H_2SO_4 is heated. This is also a laboratory method.

$$2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_3$$
$$2HNO_3 \longrightarrow H_2O + 2NO + 3O$$
$$[2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O] \text{ x } 3$$

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

(c) Nitric oxide is the first product obtained from the following two processes during the manufacture of nitric acid.

(i) Electric arc process:

By passing air through an electric arc, nitrogen and oxygen of the air combine together to form nitric oxide.

$$N_2 + O_2 \xrightleftharpoons{\text{Electric arc}} 2NO$$

(ii) Ostwald's process:

By restricted oxidation of ammonia with air in presence of platinum gauze catalyst at 750^0C, nitric oxide is formed.

$$4NH_3 + 5O_2 \xrightarrow[750^0C,\ 6atm]{\text{Pt. gauze}} 4NO + 6H_2O$$

Properties:

(a) It is a colourless gas, slightly heavier than air.
(b) It is sparingly soluble in water.
(c) It is paramagnetic indicating the presence of unpaired electron in the moleculе.
(d) It is neutral to litmus.
(e) It at once reacts with oxygen to give brown fumes of nitrogen dioxide.

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

(f) It is stable oxide. It decomposes into nitrogen and oxygen when heated at 800^0C.

$$2NO \xrightarrow{800^0C} N_2 + O_2$$

(g) It is combustible and supports combustion of boiling sulphur and burning phosphorus.

$$S + 2NO \longrightarrow SO_2 + N_2$$

(h) It dissolves in cold ferrous sulphate solution by forming a hydrated nitrosyl complex.

$$\underset{\text{Ferrous sulphate}}{[Fe(H_2O)_6]SO_4} + NO \longrightarrow \underset{\text{Hydrated nitrosyl complex (Brown colour)}}{[Fe(H_2O)_5NO]SO_4} + H_2O$$

$$\downarrow \text{ Heat}$$

$$FeSO_4 + NO + 5H_2O$$

(i) It is oxidised to nitric acid by oxidising agents like acidified $KMnO_4$ or hypochlorous acid. Thus, it acts as a reducing agent.

$$6KMnO_4 + 9H_2SO_4 + 10NO \longrightarrow 3K_2SO_4 + 6MnSO_4 + 10HNO_3 + 4H_2O$$
$$[HClO \longrightarrow HCl + O] \text{ x } 3$$
$$[NO + O \longrightarrow NO_2] \text{ x } 3$$
$$3HClO + 2NO + H_2O \longrightarrow 2NO_3 + 3HCl$$

HNO_3 oxidises nitric oxide into NO_2.

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

(j) It acts as an oxidising agent. It oxidises SO_2 to H_2SO_4 ande H_2S to S.

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

When exploded with hydrogen it liberates nitrogen.

$$2H_2 + 2NO \longrightarrow 2H_2O + N_2$$

However, when a mixture of hydrogen and nitric oxide is passed over platinum black, ammonia is formed.

$$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O$$

Stannous chloride reduces nitric oxide to hydroxylamine.

$$[SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2H] \times 3$$
$$2NO + 6H \longrightarrow 2NH_2OH$$

$$3SnCl_2 + 6HCl + 2NO \longrightarrow 3SnCl_4\ 2NH_2OH$$

(k) Nitric oxide directly combines with halogen (fluorine, chlorine, bromine) to form corresponding nitrosyl halides.

$$\underset{}{2NO} \quad + \quad \underset{(F_2,\ Cl_2\ \text{or}\ Br_2)}{X_2} \quad \longrightarrow \quad \underset{\text{Nitrosyl halide}}{2NOX}$$

Uses:

(i) In the manufacture of nitric acid.
(ii) As a catalyst in lead chamber process for the manufacture of sulphuric acid.
(iii) In the detection of oxygen to ditinguish it from nitrous oxide.

Structure:

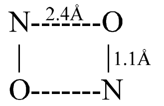
The molecule NO has eleven valnecy electrons and it is impossible for all of them to be paired.Hence, the molecule contains an odd electron which makes the gaseous nitric oxide as paramagnetic.

$$:\dot{N} \overset{\cdot\ \cdot\ \cdot}{=\!=\!=} O:$$

The structure is represented as a resonance hybrid.

$$:\dot{N}::\ddot{O}: \longleftrightarrow :\overline{N}::\overset{+}{\dot{O}}:$$

In the liquid and solid states NO is known to form a loose dimer, N_2O_2



(III) Dinitrogen Trioxide, N_2O_3

This oxide is also called nitrogen sesquioxide or nitrous anhydride.

Preparation: It is obtained by the reduction of nitric acid with arsenious oxide.

$$2HNO_3 \rightarrow H_2O + N_2O_3 + 2O$$
$$As_2O_3 + 2O \rightarrow As_2O_5$$
$$As_2O_5 + 3H_2O \rightarrow 2H_3AsO_4$$

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

It is known in pure state in solid form at very very low temperature. In the vapour state, it is present as an equimolar mixture of NO and NO_2. The mixture of NO and NO_2 may be obntained by the action of 6N nitric acid on copper.

$$2Cu + 6HNO_3 \longrightarrow 2Cu(NO_3)_2 + \underbrace{NH + NO_2}_{N_2O_3} + 3H_2O$$

(a) It condenses to a bluw coloured liquid at -30^0C. The liquid when warmed at room temperature, decomposes to a mixture of NO and NO_2 (Brown coloured)

$$\underset{\text{Blue coloured liquid}}{N_2O_3} \xrightarrow{\text{Room Temperature}} \underbrace{NO + O_2}_{\text{Brown coloured gas}}$$

(b) It is an acidic oxide. If forms nitrous acid and water and hence the name nitrous anhydride.

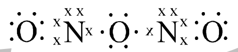
$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

The oxide combines with caustic alkali forming corresponding nitrite.

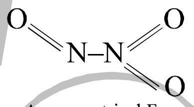
$$2NaOH + N_2O_3 \longrightarrow 2NaNO_2 + H_2O$$

Structure:

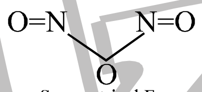
Since the oxide is unstable in liquid and gaseous states and decomposes into NO and NO_2, it may be assumed that it has the following electronic structure:

 or O=N–O–N=O

The structure is supported by its diamagnetic behaviour strucutre of N_2O_3 is of two forms:



Assymmetrical Form



Symmetrical Form

(IV) Nitrogen Dioxide, NO_2 or DInitrogen Tetroxide, N_2O_4

This oxide exists as NO_2 in gaseous state while at low temperature, it exists as a dimer N_2O_4 (Solid state)

$$\underset{\text{Brown gas}}{2NO_2} \overset{-11^0C}{\rightleftharpoons} \underset{\text{Colourless solid}}{N_2O_4}$$

Preparation: It is prespared in the laboratory either by heating nitrates of heavy metal or by the action of concentrated nitric acid on metals like copper, silver, lead etc.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

The mixture of nitrogen dioxide and oxygen is passed through a U-tube cooled by freezing mixture. Nitrogen dioxide condenses to a pale yellow liquid while oxygen escapes.

$$Zn(NO_3)_2 \longrightarrow ZnO + NO_2 + O_2$$

$$AgNO_3 \longrightarrow Ag + NO_2 + O_2$$

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

It is also obtained by air oxidation of nitric oxide.

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

Properties:

(a) It is brown colored gas wit pungent odour. Above 140^0C, it is 100%NO_2. The liquid as well as solid is entirely N_2O_4 (dimer) at low temperature. The liquid boils at 22^0C and solid melts at -11^0C.

(b) It decomposes completely into nitric oxide and oxygen at 620^0C.

$$NO_2 + HCl \longrightarrow NOCl + Cl_2 + H_2O$$

$$2NO_2 \overset{620^{o}C}{\rightleftharpoons} \underbrace{2NO + O_2}_{\text{Gaseous mixture colourless}}$$

(c) When reacted with cold water, it forms a mixture of nitrous acid and nitric acid.

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

On account of this, it is known as mixed anhydride of these two acids. However, with an excess of warm water it forms nitric acid and nitric oxide.

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

(d) When absorbed by alkalies, nitrites and nitrates are formed.

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

(e) It acts as an oxidising agent. It oxidises metals like sodium, potassium, mercury, tin copper, etc.

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

None metals like carbon, sulphur, phosphorus when burnt in its stmosphere, are converted into corresponding oxides.

$$5NO_2 + 2P \longrightarrow P_2O_5 + 5NO$$
$$2NO_2 + S \longrightarrow SO_2 + 2NO$$
$$2NO_2 + C \longrightarrow CO_2 + 2NO$$

It liberates iodine from KI and turns starch-iodide paper blue.

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

In aqueous solution, it oxidises SO_2 to sulphuric acid

$$SO_2 + H_2O + NO_2 \longrightarrow H_2SO_4 + NO$$

This reaction is used for the manufacture of H_2SO_4 by lead chamber process.

H_2S is oxidised to S and CO to CO_2.

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

(f) It behaves also as a reducing agent. It redduces ozone to oxygen.

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

It decolourises acidified $KMnO_4$ solution.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3O_2 + 5O$$
$$10NO_2 + 5H_2O + 5O \longrightarrow 10HNO_3$$

$$2KMnO_4 + 3H_2SO_4 + 10NO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 10\ HNO_3$$

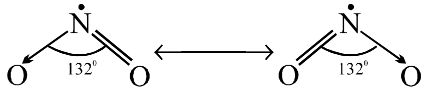
Uses

(i) It is used for the manufacture of nitric acid.

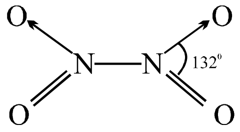
(ii) It is employed as a catalyst in the lead chamber process for the manufacture of sulphuric acid.

Structure

NO_2 molecule has V-shaped structure with O-N-O bond angle 132° and N-O bond length of about 1.19Å which is intermediate between a single and a double bond. Hence, NO_2 is regarded as a resonance hybrid of the following two streuctures.



The molecule is an odd electron molecule. The paramagnetic behaviour of NO_2 confirms this view. Due to prossession of odd eledtron, it is colored and has a tendency to polymerize to form a colour less dimer, N_2O_4. the dimer is planar in structure with N-N bond length 1.75Å.



(v) Nitrogen Pentoxide, N_2O_5

This oxide is also known as nitric anhydride.

Preparation

It is prepared by distilling concentrated nitric acid with phosphorus pentoxide in a glass apparatus.

$$\begin{array}{l} \quad 2NHO_3 \longrightarrow H_2O + N_2O_5 \\ \quad P_2O_5 + H_2O \longrightarrow 2HPO_3 \\ \hline P_2O_5 + 2HNO_3 \longrightarrow 2HPO_3 + N_2O_5 \\ \hline \end{array}$$

It is also prepared by the action of dry chlorine on solid silver nitrate at 95°C.

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

Properties

(a) It is a white crystalline solid. The crystals melt at 30°C giving a yellow liquid which decomposes at 40°C to give brown NO_2. The decompostion occurs with explosion.

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

(b) It is an acidic oxide. It reacts with water with hissing sound forming nitric acid.

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

On account of this, it is known as nitric anhydride. With alkalies if forms nitrates.

$$2NaOH + N_2O_5 \longrightarrow 2NaNO_3 + H_2O$$

(c) It acts as a strong oxidising agent. It affect organic substances such as cork, rubber, etc. It oxidises iodine readily into iodine pentoxide.

$$I_2 + 5N_2O_5 \longrightarrow I_2O_5 + 10NO_2$$

(d) With aqueous NaCl, the ionic reaction takes place.

$$N_2O_5 + NaCl \longrightarrow naNO_3 + NO_2Cl$$

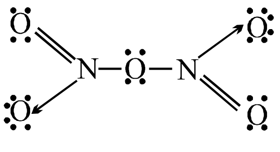
The reaction proves that N_2O_5 exists as ionic nitronium nitrate (NO_2, NO_3)

(e) N_2O_5 is decomposed by alkali metals.

$$N_2O_5 + Na \longrightarrow naNO_3 + NO_2$$

Structure

In the gaseous state, it exists as a symmetrical molecule having the structure $O_2N - O - NO_2$, N - O - N bond is almost linear. It may be represented as:



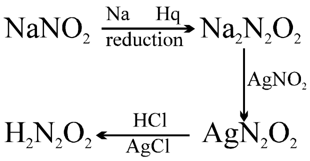
X- ray studies suggest that solid N_2O_5 is ionic in nature, i.e. nitronium nitrate, NO_2, NO_3^-.

5. Oxyacids of Nitrogen

Nitrogen forms a number of oxyacids. The most common and important oxyacids are:

(i) Hyponitrous acid, $H_2N_2O_2$

Preparation



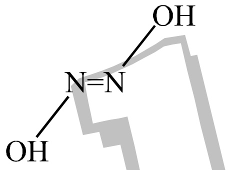
$$\begin{tikzcd} NaNO_2 \arrow[r, "Na\quad Hq", "reduction"'] & Na_2N_2O_2 \arrow[d, "AgNO_2"] \\ H_2N_2O_2 & AgN_2O_2 \arrow[l, "HCl"', "AgCl"] \end{tikzcd}$$

Properties

It is colourless, hygroscopic. It is very weak dibasic acid but a strong reducing agent.

$$H_2N_2O_2 \longrightarrow H_2O + N_2O$$

It has zero dipole moment which is based on its trans structure.



(ii) Nitrous Acid, HNO_2

The free acid is unknown. It is known only in solution.

Preparation

A solution of nitrous acid can be prepared by acidifying solutions of nitrites with mineral acids.

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$
$$KNO_2 + HCl \longrightarrow KCl + HNO_2$$

Nitrates on heating with lead decompose to give nitrite.

$$NaNO_3 + Pb \xrightarrow{\Delta} NaNO_2 + 2HNO_2$$

An aqueous solution of the acid, free from any salt, can be prepared by treating barium nitrite with calculated amount of dilute sulphuric acid. Singce the acid is very unstable, the reaction is carried out at low temperature (freezing mixture temperature). The insoluble barium sulphate is filtered off.

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

A solution of nitrous acid may also the prepared by dissolving N_2O_3 in water.

$$HNO_2 + NaOH \longrightarrow NaNO_2 + H_2O$$
$$NH_3 + H_2O_2 \longrightarrow HNO_2 + H_2O$$

Properties

(a) Aqueous solution of nitrous acid is pale blue. This is due to the presence of nitrogen trioxide, N_2O_3 the colour fades on standing for sometime.

(b) It is weak acid and reacts with alkalies to form salts known as nitrites.

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

(c) **Auto-oxidation**

The acid is unstable and even in cold solution, it undergoes auto-oxidation.

$$\begin{array}{l} 2HNO_2 \longrightarrow 2NO + H_2O + O \\ \quad HNO_2 + O \longrightarrow HNO_3 \\ \hdashline 2HNO_2 \longrightarrow 2NO + HNO_3 + H_2O \\ \hdashline \end{array}$$

On heating, it decomposes into nitric oxide and nitrogen dioxide.

$$2HNO_2 \longrightarrow H_2O + \underset{\underset{NO + \underset{(brown)}{NO_2}}{\rightleftharpoons}}{N_2O_3}$$

(d) Oxidising nature

It acts as an oxidising agent due to ease with which it decomposes to give nascent oxygen. the potential equation when it acts as an oxidising agent is:

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

(i) Iodine is liberated from potassium iodide.

$$2KI + H_2SO_4 + 2HNO_2 \longrightarrow K_2SO_4 + 2NO + I_2 + 2H_2O$$

(ii) Stannous chloride is oxidised to stannic chloride.

$$SnCL_2 + 2HCL + 2HNO_2 \longrightarrow SnCl_4 + 2NO + 2H_2O$$

(iii) Sulphur chloride is oxidised to sulphuric acid.

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

(iv) Sulphur is formed by oxidation of hydrogen sulphide.

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

(v) Acidified ferrous sulphate is oxidised to ferric sulphate.

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

(vi) Sodium arsentie is oxidised to sodium arsenate.

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

(e) Reducing nature

Nitrous acid acts as a reducing agent as it can be oxidised into nitric acid.

$$HNO_2 + O \longrightarrow HNO_3$$

(i) It reduces bromine to hydrobromic acid.

$$Br_2 + H_2O + HNO_2 \longrightarrow 2HBr + HNO_3$$

(ii) Acidified potassium permanganate is decolourised.

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

(iii) Acidified potassium dichromate is reduced to chromic sulphate (green)

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

(iv) Hydrogen peroxide is reduced to water

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

(f) Reaction with ammonia

It reacts with ammonia to form nitrogen and water.

$$NH_3 + HNO_2 \longrightarrow \underset{\text{Intermediate}}{[NH_4NO_2]} \longrightarrow N_2 + 2H_2O$$

(g) Reaction with urea

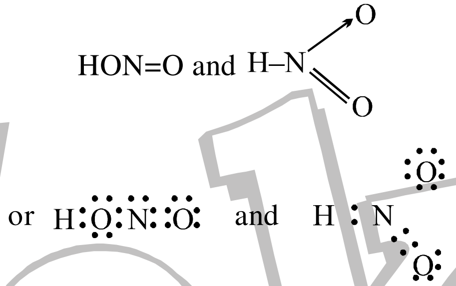
It decomposes urea and aliphatic primary amines to nitrogen

$$\underset{\text{Urea}}{NH_2CONH_2} + 2HNO_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + HO\,.\,NO \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + N_2 + H_2O$$

Structure

Since nitrous acid forms two types of organic derivatives, the nitrites (R-ONO) and nitro compounds (R-NO_2), it is considered to be a automeric mixture ot two forms.



(iii) Nitric acid, HNO_3

It was named aqua fortis (means strong water) by alchemists.

Preparation

(i) Laboratory Method

$$KNO_3 + \text{conc. } H_2SO_4 \longrightarrow KHSO_4 + HNO_3(\text{vap})$$

vapours of nitric acid evolved are condensed in a glass receiver.

(ii) Industrial Preparation

(A) Birkeland Eyde Process or arc process

step 1 $\quad N_2 + O_2 \xrightarrow[\text{Electric Arc}]{3000^0 C} 2NO - \text{heat}$

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

step 3 $\quad NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

step 4 $\quad HNO_2 \longrightarrow HNO_3 + NO + H_2O$

(B) Ostwald's Process

step 1 $\quad NH_3 + O_2 \xrightarrow[700-800^0 C]{\text{Pt. gauze}} NO + H_2O + \text{heat}$

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

step 3 $\quad NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

step 4 $\quad HNO_2 \longrightarrow HNO_3 + NO + H_2O$

Properties

Physical

Nitric acid usually acquires yellow colour due to its decomposition by sunlight into NO_2.

$$4HNO_3 \xrightarrow{\text{Sunlight}} 4NO_2 + 2H_2O + O_2$$

The yellow colour of the acid can be removed by warming it to 60-80°C and bubbling dry air through it. It has extremely corrosive action on the skin and causes painful sores.

Chemical

(a) It is very strong acid. It exhibits usual properties of acids. It reacts with basic oxides, carbonates, bicarbonates and hydroxides forming corresponding salts.

$$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$
$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$
$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

(b)Oxidising nature : Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

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

or $$2HNO_3 \longrightarrow H_2O + 2NO + 3O$$

(i) Oxidation of non-metals: The nascent oxygen oxidises various non-metals to their corresponding highest oxyacids.

(1) Sulphur is oxides to sulphuric acid

$$S + \underset{\text{conc.and hot}}{6HNO_3} \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

(2) Carbon is oxidised to carbonic acid

$$C + 4HNO_3 \rightarrow H_2CO_3 + 4NO_2 + 2H_2O$$

(3) Phosphorus is oxidised to orthophosphoric acid.

$$2P + \underset{\text{conc. and hot}}{10HNO_3} \rightarrow 2H_3PO_4 + 10NO_2 + 2H_2O$$

(4) Iodine is oxidised to iodic acid

$$I_2 + \underset{\text{conc. and hot}}{10HNO_3} \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

(ii) Oxidation of metalloids

Metalloids like non-metals also form highest oxyacids

(1) Arsenic is oxidised to arsenic acid

$$2As + 10HNO_3 \rightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O$$

or $$As + \underset{\text{conc. and hot}}{5HNO_3} \rightarrow H_3AsO_4 + 5NO_2 + H_2O$$

(2) Antimony is oxidised to antimonic acid

$$Sb + \underset{\text{conc. and hot}}{5HNO_3} \rightarrow H_3SbO_4 + 5NO_2 + H_2O$$

(3) Tin is oxidised to meta-stannic acid.

$$Sn + 2HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$$

(iii) Oxidation of Compounds:

(1) Sulphur dioxide is oxidised to sulphuric acid

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

(2) Hydrogen sulphiode is oxidised to sulphur

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

(3) Ferrous sulphate is oxidised to ferric sulphate in presence of H_2SO_4

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

(4) Iodine is liberated from KI.

$$6KI + 8HNO_3 \rightarrow 6KNO_3 + 2NO + 3I_2 + 4H_2O$$

(5) HBr, HI are oxidised to Br_2 and I_2, respectively.

$$2HBr + 2HNO_3 \rightarrow Br_2 + 2NO_2 + 2H_2O$$

Similarly, $2HI + 2HNO_3 \rightarrow I_2 + 2NO_2 + 2H_2O$

(6) Ferrous sulphide is oxidised to ferrous sulphate

$$FeS + HNO_3 \rightarrow FeSO_4 + 8NO_2 + 4H_2O$$

(7) Stannous chloride is oxidised to stannic chloride is presence of HCl.

$$2HNO_3 + 14H \rightarrow \underset{\text{Hydroxylamine}}{NH_2OH} + NH_3 + 5H_2O$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

$$7SnCl_2 + 14HCl + 3HNO_3 \rightarrow 7SnCl_4 + Nh_2OH + NH_4NO_3 + 5H_2O$$

(8) Cane sugar is oxidised to oxalic acid.

$$C_{12}H_{22}O_{11} + 36HNO_3 \rightarrow 6(COOH)_2 + 36NO_2 + 23H_2O$$

(c) Action on Metals: Most of the metals will the exveption of noble metals like gold and platinum are attacked by Nitric acid plays a double role in the action of metals, i,e, it acts as an acid as well as an oxidising agent. ARmstrong postulated that primary action of nitric acid is to produce hydrogen in the nascent form. Before this hydrogen is allowed to escape, it reduces the nitric acid into number of products like NO_2, NO, N_2O, N_2 or NH_3 according to the following reactions:

$$\text{Metal} + HNO_3 \longrightarrow \text{Nitrate} + H$$
$$2HNO_3 + 2H \longrightarrow 2NO + 2H_2O$$
$$2HNO_3 + 6H \longrightarrow 2NO + 4H_2O$$
$$2HNO_3 + 10H \longrightarrow N_2 + 6H_2O$$
$$2HNO_3 + 16\,H \longrightarrow 2NH_3 + 6H_2O$$

The progress of the reaction is controlled by a number of factors:

(a) the nature of the metal,
(b) the concentration of the acid,
(c) the temperature of the reaction,
(d) the presence of other impurities.

Concentration of nitric acid	Metal	Main Products
Very dilute HNO_3 (6%)	Mg, Mn	H_2 + Metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate + H_2O
Dilute HNO_3 (20%)	Pb, Cu, Ag, Hg	NO + metal nitrate + H_2O
	Fe, Zn	N_2O + metal nitrate + H_2O
	Sn	NH_4NO_3 + $Sn(NO_3)_2$
Conc. HNO_3(70%)	Zn, Fe, Pb, Cu, Ag	NO_2 + metal nitrate + H_2O
	Sn	NO_2 + H_2SnO_3 Metastannic acid

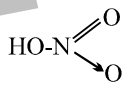
Action on Proteins

(i) Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.

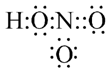
(ii) **Oxidation** A number of organic compounds are oxidised.
Sawdust catches fire when nitric acid is poured on it. Turpentine oil bursts into flames when treated with fuming nitric acid. Cane sugar is oxidised to oxalic acid. Toluene is oxidised to benzoic acid with dil. HNO_3.

Structure

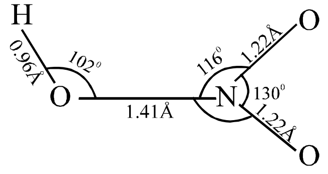
Nitric acid is a monobasic acid, i.e., the molecule consist of one hydroxyl group as it is formed by the hydrolysis of nitryl chloride, NO_2Cl. It may be structurally represented as below:



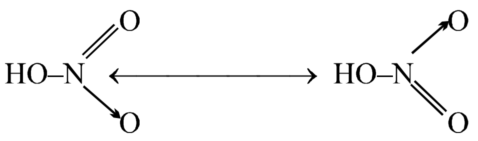
or



Gaseous nitric aicd is a planar molecule. The bond lengths and bond angles as present in the molecule are represented in the figure:



It is supposed to exist in two resonting forms.



PHOSPHORUS

It glows in the dark and was, therefore, called phosphorus (Greek work, phos=light, and phero=1 carry)

Occurrence

Since phosphorus is an active element, it is not found free in nature. It is widely distributed in nature in the combined state. It occurs as phosphates in the rocks and in the soil and as phosphoproteins in all living beings. It is an essential constituents of bones, teeth, blood and nervous tissure. It is necessary for the growth of plants. Bone ash contains about 80% calcium phosphate. it is present in milk, eggs and guano (excreta of seabirds). The principal minerals of phosphorous are

(i) Phosphorite	$Ca_3(FO_4)_2$
(ii) Fluorapatite	$3Ca_3(PO_4)_2.CaF_2$
(iii) Chlorapatite	$3Ca_3(PO_4)_2.CaCl_2$

Extraction

Phosphorus is extracted either from phosphorite or bone ash by the application of following two processes.

(i) Retort process or old process.
(ii) Electrothermal process or modern process.

(i) Retort process or old process

The phosphorite mineral or bone ash is digested with concentrated sulphuric acid (about 60%). Insoluble calcium sulphate and orthophosphoric acid are formed.

$$Ca(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 3H_3PO_4$$

The syrupy liquid is separated from insoluble residue by filtration. The liquid is evaporated when it changes into metaphosphoric acid with evolution of water.

$$H_3PO_4 \rightarrow \underset{\text{Metaphosphoric acid}}{HPO_3} + H_2O$$

The metaphosphoric acid is mixed with powdered coke and distilled in fireclay retorts at a bright red het. The acid is reduced to phosphorus by carbon which comes in vaporized form. The vapours are condensed below water.

$$4HPO_3 + 10C \rightarrow P_4 + 10CO + 2H_2O$$

(ii) Electrothermal process or modern process.

The mixture of phosphorite, carbon and silica is dried and then introduced into the electric furnace. The furnace is an iron tank lined inside with refractory bricks. Carbon electrodes are fitted on either side of the furnace. The furnace has two exits, one for removal of vapours in the upper part of the furnace and the other for removal of slag in the lower part of furnace. The charge is introduced through the closed hopper arrangement.

The mixture is heated at 1400-1500°C by the discharge of an alternating current between carbon electrodes. Silica combines with calcium phosphate and forms phosphorus pentaxide which is reduced by carbon into phosphorus.

$$[Ca_3(PO_4)_2 + 2SiO_2 \rightarrow 3CaSiO_3 + P_2O_5] \times 2$$
$$2P_2O_5 + 10C \rightarrow P_4 + 10CO$$

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10COs$$

Vapours of phosphorus and carbon monoxide leave the furnace through the upper exit and are condensed under water. The liquid slag is tapped out periodically through an exit in the base.s

Purification

Phosphorus obtained is further purified by melting under acidified potassium dichromate solution when the impurities are oxidised. It is redistilled.

Allotropic modifications of phosphorus

Phosphorus exists in a number of allotropic forms. These forms are:

(i) Yellow or white phosphorus
(ii) Red phosphorus
(iii) Scarlet phosphorus
(iv) α-black phosphorus
(v) β-black phosphorus
(vi) violet phosphorus

The main allotropic forms, however, are white and red.

White or yellow phosphorus

This is the common variety and is obtained by the methods described above. This form is chemically very active.

Properties

(a) The pure form is white but attains yellow colour on long standing due to the formation of a thin film of the red variety on the surface.

(b) It is a transparent waxy solid (sp. gr. 1.8) and can be easily cut with knife.

(c) It has characteristic garlic smell and is poisonous in nature. 0.15 g is the fatal dose. Vapours are also injurious. Persons working with phosphorus develop a disease in which the jaw bones decay. This disease is known as **phossy jaw.**

(d) It is insoluble in water but readily soluble in carbon disulphide.

(e) It melts at 44°C into a yellow liquid. It boils at 280°C.

(f) In contact with air, it undergoes slow combustion and glows dark. ths property is called phosphorescence.

(g)Its ignition temperature is low (about 30°C). It readily catches fire giving dense fumes of phosphorus pentoxide. it si, therefore, kept in water.

$$P_4 + 5O_2 \rightarrow P_4O_{10} \text{ or } 2O_2O_5$$

(h) It dissolves in caustic alkalies on boiling in an inert atmosphere and forms phosphite.

$$P_4 + \underset{\substack{\text{Caustic}\\\text{soda}}}{3NaOH} + 3H_2O \rightarrow \underset{\substack{\text{sodium}\\\text{hypophosphite}}}{3NaH_2PO_2} + PH_3 \uparrow$$

(i) It directly combines with halogens forming first trihalides and then pentahalides.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3; \quad P_4 + 10Cl_2 \rightarrow 4PCl_5$$

(j) It combines with a number of metals forming phosphides.

$$6Mg + P_4 \rightarrow 2Mg_3P_2 \text{(Magnesium phosphide)}$$
$$6Ca + P_4 \rightarrow 2Ca_3P_2 \text{ (Calcium phosphide)}$$

(k) It combines with sulphur with explosive violence forming a number of sulphides such as P_2S_3, P_2S_5, P_4S_3 and P_4S_7.

(l) It acts as a strong reducing agent. It reduces nitric acid and sulphuric acid.

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$
$$P_4 + 10H_2SO_4 \rightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$$

It reduces solutions of copper, silver and gold salts to corresponding metals,

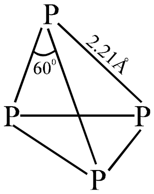
$$P_4 + 10CuSO_4 + 16H_2O \rightarrow 10Cu + 4H_3PO_4 + 10H_2SO_4$$

When the solution is heated, cuprous phosphide is formed.

$$3P_4 + 12\ CuSO_4 + 24\ H_2O \xrightarrow{\text{heat}} 4Cu_3P + 8H_3PO_3 + 12H_2SO_4$$
$$P_4 + 20AgNO_3 + 16H_2O \rightarrow 20Ag + 4H_3PO_4 + 20HNO_3$$

(m) when heated in inert atmosphere at 240°C, it changes into red variety.

$$\text{Yellow P} \xrightarrow[\text{Inertatm.}]{240-250^{o}\,C} \text{Red P}$$



(n) Structure

The vapour density of white phosphorus between 500-700°C, is 62 which corresponds to the molecular formula P_4. The four phosphorus atoms lie at the corners of a regular tetrahedron. Each phosphorus atom is linked to each of the other three atoms by covalent bonds. The P-P bond length is equal to 2.21Å. The bond angle is equal to 60° which suggests that he molecule is under strain and hence active in nature.

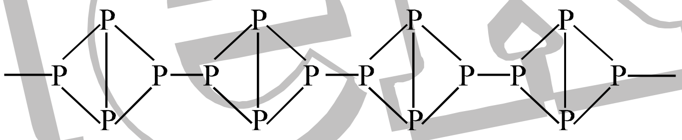
Red Phosphorus

Preparation

Red phosphorus is formed by heating yellow phosphorus, between 240-250°C, in presence of an inert gas. The heating is done in an egg shaped iron vessel provided with a upright tube closed by safety value. the thermometers placed in iron tubes help to regulate the temperature.

Structure of red phosphorus

The exact structure of red phosphorus is not yet known. It is regarded as a polymer consisting of chains of P_4 tetrahedral linked together possible in the manner as shown in the figure.



Proposed molecular structure of red phophorus

Comparison between White and Red Phosphorus

S.No.	Property	White Phosphorus	Red Phosphorus
1.	Physical State	Soft waxy solid	Brittle powder
2.	Colour	White when pure. Attains yellow colour on standing	Red
3.	Odour	Garlic	Odourless
4.	Specific gravity	1.8	2.1
5.	Melting point	44°C	Sublimes in absence of air at 290°C
6.	Ignition temperature	Low, 30°C	High, 260°C
7.	Solubility in water	Insoluble	Insoluble
8.	Solubility in CS_2	Soluble	Insoluble
9.	Physiological action	Poisonous	Non-poisonous
10.	Chemical activity	Very active	Less active
11.	Stability	Unstable	Stable

12.	Phosphorescence	Glows in dark	Does not glow in dark
13.	Burning in air	Forms P_4O_{10}	Forms P_4O_{10}
14.	Reaction with NaOH	Evolves phosphine	No action
15.	Action of Cl_2	Combines spontaneously to form PCl_3 & PCl_5	Reacts on heating to form PCl_3 & PCl_5
16.	Reaction with hot HNO_3	Forms H_3PO_4	Forms H_3PO_4
17.	Molecular formula	P_4	Complex Polymer

Uses of phosphorus

(i) It is largely used in the match industry. Red phosphorus or scarlet phosphorus is preferred to yellow variety.

(ii) Yellow phosphorus is used as a rat poison.

(iii) Red phosphorus is used for the preparation of HBr and HI.

(iv) Radioactive phosphorus (P^{32}) is used in th treatement of leukemia and other blood disorders.

(v) It is used for making incendiary bombs and smoke screens.

(vi) It is used in the manufacture of phosphor bronze, an alloy of phosphorus, copper and tin.

(vii)It is used in the manufacture of compounds like hypophosphites (medicine), phosphorus chlorides in industry, calcium phosphide used in making Holme's signals and orthophosphoric acid.

Compouns of Phosphorus

1. Phosphine, PH_3

It is analogous to ammonia.

Laboratory preparation

It is prepared by blining yellow phosphorus with a concentrated solution of solution of sodium hydroxide in an inert atmosphere.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{sodium hypophosphite}}{3NaH_2PO_2} + PH_3$$

Besides PH_3, small amounts of hydrogen and phosphorus dihydride (P_2H_4) are also formed.

$$P_4 + 4NaOH + 4H_2O \rightarrow 3NaH_2PO_2 + 2H_2$$
$$3P_4 + 8NaOH + 8H_2O \rightarrow 8NaH_2PO_2 + 2P_2H_4$$

As soon as the bubbles of the gas come in contact with air, they catch fire spontaneously forming rings of smoke known as vortex rings. This combustion is due to the presence of highly inflammable phosphorus dihydride (P_2H_4).

$$2P_2H_4 + 7O_2 \rightarrow \underset{\text{Metaphosphoric acid}}{4HPO_3} + 2H_2O$$

P_2H_4 can be removed from phosphine by the following methods:

(i) By passing the evolved gas through a freezing mixture which condenses P_2H_4.

(ii) By passing the gas through HI. PH_3 is absorbed forming phosphonium iodide. This on treatment with casutic potash gives pure phosphine.

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3$$

Physical properties

It is a colourless gas having unpleasant garlic like odour or rotten fish odour.

(a) Decomposition

When heated out of contact of air to 440^{O}C or when electric sparks are passed through, phosphine decomposes into red phosphorus and hydrogen.

$$PH_3 \rightarrow P_4 + 6H_2$$

(b) Combustibility

A pure sample of phosphine is not spontaneously inflammable. It burns in air or oxygen when heated at 150^{o}C.

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$$

The spontaneous in flammability of phosphine at the time of preparation is due to the presence of highly inflammable phosphorus dihydride, P_2H_4. This property is used in making Holme's signal. A mixture of calcium carbide and calcium phosphide is placed in metallic containers. Two holes are made and the container is thrown into the sea. Water enters and produces acetylene and phosphine respectively. The gaeous mixture catches fire spontaneously due to the presence of P_2H_4. The acetylene produces a bright luminous flame which serves as a signal to the approaching ship.

(c) Action of chlorine

Phosphine burns in the atmosphere of chlorine and forms phosphorus pentachloride.

$$PH_3 + 4Cl_2 \rightarrow PCl_5 + 3HCl$$

(d) Basic nature

Phosphine is neutral to litmus. However, it si a weak base, even weaker than ammonia. It reacts with HCl, HBr or HI to form phosphonium compounds.

$PH_3 + HCl \rightarrow PH_4Cl$ (Phosphonium chloride)

$PH_3 + HBr \rightarrow PH_4Br$ (Phosphonium bromide)

$PH_3 + HI \rightarrow PH_4I$ (Phosphonium iodide)

(e) Action of nitric acid

In contact with nitric acid phosphine begins to burn.

$$2PH_3 + 16\,HNO_3 \rightarrow P_2O_5 + 16NO_2 + 11H_2O$$

(f) Addition compounds

In forms addition compounds with anhydrous $AlCl_3$ and $SnCl_4$

$$AlCl_3 + 2PH_3 \rightarrow AlCl_3.2PH_3$$

$$SnCl_4 + 2PH_3 \rightarrow SnCl_4.2PH_3$$

When PH_3 is passed through cuprous chloride solution in HCl, it forms an addition compound.

$$Cu_2Cl_2 + 2PH_3 \rightarrow 2CuCl.\,PH_3$$

(g) Formation of phosphides

(i) When phosphine is passed through copper sulphate solution, a black precipitate of cupric phosphide is formed.

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$

(ii) A black precipitate of silver phosphide is formed when phosphine is circulated through silver nitrate solution.

$$3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$$

(h) The mixture of PH_3 and N_2O or PH_3 and NO explodes in presence of electric spark.

$$PH_3 + 4N_2O \rightarrow H_3PO_4 + 4N_2$$

2. Oxides of Phosporus

Phosphorus forms three important oxides. These exist in dimeric forms.

(i) Phosphorus trioxide, P_2O_3 or P_4O_6
(ii) Phosphorus tetroxide, P_2O_4 or P_4O_8
(iii) Phosphorus pentoxide, P_2O_5 or P_4O_{10}

(i) Phosphorus trioxide P_2O_3 or P_4O_6

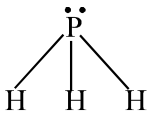
It is formed by burning phosphorus in limited supply of air.

$$P_4 + 3O_2 \rightarrow P_4O_6$$

The pentoxide, formed in small amount, is removed by passing through glass wool. The vapours of trioxide pass through the glass wool and are condensed in a reveiver cooled by a freezing mixture.

Structure of Phosphine

Phosphine is a covalent molecule. It has pyramidal structure like ammonia.



The bond angle H-P-H is 93°.

Uses:

(i) For making Holme's signals.
(ii) For making smoke screens.
(iii) For making metallic phosphides.

Vapours of phosphorus at low pressure react with N_2O at 600°C to form P_2O_3.

$$P_4 + 6N_2O \xrightarrow{600^\circ C} 2P_2O_3 + 6N_2$$

Properties

(a) It is a waxy solid having garlic odour.
(b) It is poisonous in nature.
(c) It is soluble in benzene or chloroform.
(d) When heated above 210°C, it forms red phosphorus and another oxide, P_4O_8.

$$4P_4O_6 \rightarrow \underset{\substack{\text{Phosphorus}\\ \text{tetroxide}}}{3P_4O_8} + \underset{\text{Red}}{4P}$$

When heated at about 440°C, it dissociates to phosphorus dioxide.

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

(e) In contact with air, it is oxidised to phosphorus pentoxide.

$$P_4O_6 + 2O_2 \rightarrow P_4O_{10}$$

(f) It burns in chlorine forming oxy-chlorides.

$$P_4O_6 + 4Cl_2 \rightarrow \underset{\substack{\text{Phosphorus}\\ \text{Oxy-chloride}}}{2POCl_3} + \underset{\substack{\text{Metaphosphorus}\\ \text{Oxy-chloride}}}{2PO_2Cl}$$

(g) In cold water it dissolves slowly forming phosphorus acid.

$$P_4O_6 + 6H_2O\ (\text{cold}) \rightarrow 4H_3PO_3$$

With hot water, a violent reaction occurs forming orthophosphoric acid and phosphine.

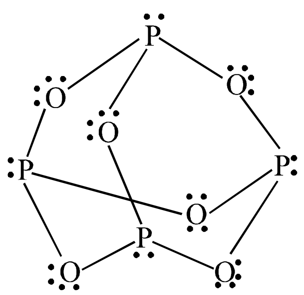
$$P_4O_6 + 6H_2O\ (\text{hot}) \rightarrow 3H_3PO_4 + PH_3$$

The above reaction is actually the conversion of phosphorus acid into orthophosphoric acid and phosphine.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

This oxide is known as acid anhydride of phosphorus acid.

Structure of phosphorus trioxide



(ii) Phosphorus pentoxide, P_4O_{10}

It is prepared by heating phosphorus in a free supply of air or oxygen.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

It is further purified by sublimation.

Phosphorus burns in CO_2 at 100°C to form P_2P_5.

$$2P + 5CO_2 \rightarrow P_2O_5 + 5CO$$

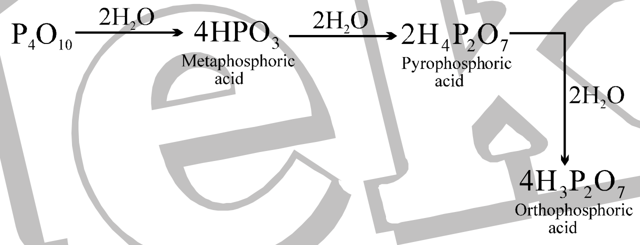
Properties

(a) It is a white crystalline compounds

(b) It is odourless when pure. The usual garlic odour is due to presence of small amount of P_4O_6 as impurity.

(c) It sublimes on heating.

(d) It has great affinity for water. The final product is orthophosphoric acid. It is therefore, termed phosphoric anhydride.



$$\text{i.e.}P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

It is, thus used as a powerful dehydrating or drying agent. It removes water from inorganic and organic compounds like H_2SO_4, HNO_3, RCOOH, $RCONH_2$, etc.

$$2H_2PO_4 + P_4O_{10} \rightarrow 2SO_3 + 4HPO_3$$
$$4HNO_3\ P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$$
$$4CH_3{}^{-}COOH + P_4O_{10} \rightarrow 2(CH_3CO)_2O + 4HPO_3$$
$$2CH_3CONH_2 + P_4O_{10} \rightarrow 2CH_3Cn + 4HPO_3$$

It also chars wood, paper, sugar etc.

(e) when heated strongly with carbon, it forms red phosphorus.

$$P_4O_{10} + 10C \rightarrow 10CO + 4P(\text{red phosphorus})$$

(f) when fused with basic oxides, it forms phosphates.

$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

(g) 30% H_2O_2 react on P_2O_5 in acetonitrile solution at low temperature to form peroxy monophosphoric acid.

$$P_2O_5 + 2H_2O_2 + H_2O \rightarrow 2H_3PO_5$$

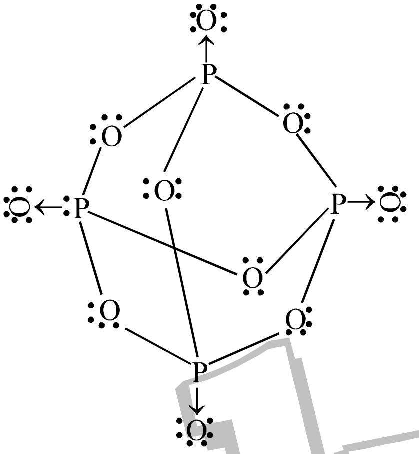
(h) Mixture of P_2O_5 and O_2 in vapour state combine in presence of electric discharge to form P_2O_6 called phosphorus peroxide.

$$P_2O_5 + 1/2O_2 \rightarrow P_2O_6$$

Uses

It is most effective drying or dehydrating agent below 100°C

Structure of phosphorus pentoxide



3. Oxyacids of phosphorus

Phosphorus forms a number of oxyacids. Common oxyacids are given below.

Name of Oxyacid	Formula	Basicity	Oxidation state of P
Hydrophosphorus acid	H_3PO_2	1	+1
Phosphorus acid	H_3PO_3	2	+3
Orthophosphoric acid	H_3PO_4	3	+5
Metaphosphoric acid	HPO_3	1	+5
Hypophosphoric acid	$H_2P_2O_6$	4	+4
Pyrophosphoric acid	$H_4P_2O_7$	4	+5

(i) Phosphorus acid, H_3PO_3, Prepartion

(i) It is obtained by dissolving phosphorus trioxide in water.

$$P_4O_6 + 6H_2O \rightarrow H_3PO_3$$

(ii) It is also obtained by hydrolysis of phosphorus trichloride.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

Chlorine is passed over molten white phosphorus under water when phosphorus trichloride formed undergoes hydrolysis.

$$2P + 3Cl_2 \rightarrow 2PCl_3$$

The solution is heated until the temperature becomes 180°C. On cooling crystals of phosphorus acid are obtained.

Properties

(a) It is colourless crystalline compound. It melts at 73°C. It is highly soluble in water.

(b) When heated, it forms orthophosphoric acid and phosphine.

$$4H_3PO_3 \xrightarrow{200^\circ C} 3H_3PO_4 + PH_3$$

(c) It si strong acid. It is diabasic in nature.

$$H_3PO_3 \Leftrightarrow H^- + H_2PO_3^- \Leftrightarrow 2H^- + HPO_3^-$$
$$K_1 = 10^{-1};\ K_2 = 2 \times 10^{-7}$$

It thus forms two series of salts such as NaH_2PO_3 adn Na_2HPO_3 known as primary phosphites and secondary phosphites respectively.

(d) It acts as a strong reducing agent. The potential equation is:

$$H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2H$$

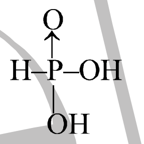
It reduces $CuSO_4$ to Cu, $AgNO_3$ to Ag, $HgCl_2$ to Hg_2Cl_2, I_2 to HI and acidfied $KMnO_4$ solution.

$$\begin{array}{l} CuSO_4 + 2H \rightarrow Cu + H_2SO_4 \\ AgNO_3 + H \rightarrow Ag + HNO_3 \\ 2HgCl_2 + 2H \rightarrow Hg_2Cl_2 + 2HCl \\ I_2 + 2H \rightarrow 2HI \end{array}$$

$$\begin{array}{l} 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \\ [H_3PO_3 + O \rightarrow K_3PO_4] \times 5 \\ \hline 2KMnO_4 + 3H_2SO_4 + 5H_3PO_3 \rightarrow K_2SO_4 + 2MnSO_4 + 5H_3PO_4 + 3H_2O \end{array}$$

Structure of Phosphorus acid

It is diabasic acid, i.e. two hydrogen atoms are insoluble or two hydroxyl groups are present. Thus, the structure is:



$$H-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH$$

The phosphorus lies in sp^3 hybrid state.

(ii) Orthophosphoric aicd, H_3PO_4

This acid is commonly called as phosphoric acid.

Preparation

(i) It is formed when phosphorus pentoxide is boiled with hot water.

(ii) ORthophosphoric acid is also formed when PCl_5 (Phosphorus pentachloride) is boiled with water.

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

(iii) Laboratory preparation

The best method for its preparation in the laboratory is to heat red phosphorus with concentrated nitric acid in a flask with a reflux condenser.

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

The reaction is usually carried out is presence of a crystal of iodine. The iodine acts as a catalyst.

$$\begin{array}{l} P + 3I \rightarrow PI_3 \\ PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI \\ 3HI + 3HNO_3 \rightarrow 3H_2O + 3NO_2 + 3I \\ H_3PO_3 + 2HNO_3 \rightarrow H_3PO_4 + H_2O + 2NO_2 \\ \hline P + 5HNO_3 \rightarrow H_3PO_4 + 5NO_2 + H_2O \end{array}$$

The solution is concentrated till it becomes syrupy about 170°C. It is cooled over conc. H_2SO_4 in vacuum dessicator when crystals of orthophosphoric acid are formed.

Manufacture

It is prepared on large scale from bone ash or phosphoric mineral.

(a) By decomposing calcium phosphate present is bone ash or phosphoric meneral with conc. H_2SO_4.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$$

On standing calcium sulphate settles down and the clear supernatant liquid separates out. The liquid is concentrated when about 85% concentrated orthophosphoric acid is obtained.

(b) The bone ash is dissolved in minimum amount of nitric acid and lead acetate is added as to precipitate lead phosphate. The lead salt is then decomposed by passing H_2S.

$$Pb_3(PO_4)_2 + 3H_2S \rightarrow \underset{\text{insoluble}}{3PbS} + \underset{\text{solution}}{2H_3PO_4}$$

(c) Bone ash or calcium phosphate is converted into phosphorous pentoxide when heated with silica in electric furnace.

$$2Ca_3(PO_4)_2 + 6SiO_2 \rightarrow 6CaSiO_3 + P_4O_{10}$$

P_4O_{10} is then dissolved in hot water.

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

properties

(a) It is transparent deliquescent solid. It melts at 42.3°C. It absorbs water and forms colourless syrupy mass. It is highly soluble in water.

(b) Heating effect

When heated at 250°C, it is converted into pyrophosphoric acid.

$$2H_3PO_4 \xrightarrow{250^{o}C} H_4P_2O_7 + H_2O$$

On further heating, it is converted into metaphosphoric acid.

$$H_3PO_4 \xrightarrow[600^{o}C]{\text{heat}} HPO_3 + H_2O$$

$$H_4P_2O_7 \xrightarrow{\text{heat}} 2HPO_3 + H_2O$$

When strongly heated at red heat, it forms P_4O_{10}.

(c) Acidic mature

It is tribasic acid, i.e. all the three hydrogen atoms are ionizable. It forms three series of salts.

$$H_3PO_4 \Leftrightarrow H^+ + H_2PO_4^- \Leftrightarrow 2H^+ + HPO_4^{2-} \Leftrightarrow 3H^+ + PO_4^{3-}$$

$$\underset{\text{(primary salt)}}{NaH_2PO_4} \qquad \underset{\text{(secondary salt)}}{Na_2HPO_4} \qquad \underset{\text{(normal salt)}}{Na_3PO_4}$$

Primary salt on heating forms a slat of metaphosphoric acid.

$$\underset{\text{Sodium dihydrogen phosphate}}{NaH_2PO_4} \xrightarrow{\text{heat}} \underset{\text{Sodium metaphosphate}}{NaPO_3} + H_2O$$

Secondary salt on heating forms a slat of pyrophosphoric acid.

$$\underset{\text{Disod.Hydrogen phosphate}}{2Na_2HPO_3} \xrightarrow{\text{heat}} \underset{\text{Sodium pyrophosphate}}{Na_4P_2O_7} + H_2O$$

Normal salt is not affected by heating.

In case, ammonium ion is present in the slat it behaves as hydrogen.

$$2MgNH_4PO_4 \xrightarrow{\text{heat}} Mg_2P_2O_7 + 2NH_3 + H_2O$$

$$NaNH_4HPO_4 \xrightarrow{\text{heat}} naPO_3 + NH_3 + H_2O$$

(d) Reaction with $AgNO_3$

A yellow precipitate of silver phosphate is formed.

$$3AgNO_4 + H_3PO_4 \rightarrow \underset{\text{yellow ppt.}}{Ag_3PO_4} + 3HNO_3$$

(e) Reaction with $BaCl_2$

A white ppt. of barium phosphate is formed in neutral or alkaline solution.

$$3BaCl_2 + 2H_3PO_4 \rightarrow \underset{\text{white ppt.}}{Ba_3(PO_4)_2} + 6HCl$$

(f) Reaction with bromides and iodides

Hydrobromic and hydroiodic acids are liberated from bromides and iodides respectively. This is te laboratory preparation of HBr and HI.

$$3NaBr + H_3PO_4 \rightarrow Na_3PO_4 + 3HBr$$
$$3NaI + H_3PO_4 \rightarrow Na_3PO_4 + 3HI$$

(g) Reaction with magnesium salt

Magnesium slats combine with orthophosphoric acid in presence o ammonium chloride nd ammonium hydroxide to form a white precipitate of magnesium ammonium phosphate.

$$MgSO_4 + NH_4Cl + H_3O_4 \rightarrow Mg(NH_4)PO_4 + H_2SO_4 + HCl$$

This reaction is used to test Mg^{2+} ion.

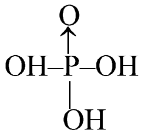
(h) On heating orthophosphoric acid is presence of nitric acid with ammonium molybdate a canary yellow ppt. of ammonium phosphomolybdate is formed.

$$H_3PO_4 + 21\ HNO_3 + 12\ (NH_4)_2\ MoO_4 \rightarrow \underset{\text{Ammoniumphosphomolybdate}}{(NH_4)_3PO_4 12MoO_3} + 21\ NH_4NO_3 + 12\ H_2O$$

This reaction is used to test PO_4^{3-} ion.

Structure of orthophosphoric acid

Orthophosphoric acid is a tribasic. i.e. 3 hydroxyl groups are present. The structure of the acid is thus represented as:



$$\begin{array}{c} O \\ \uparrow \\ OH\text{–}P\text{–}OH \\ | \\ OH \end{array}$$

Phosphorus atom lies in sp^3 hybrid state.

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