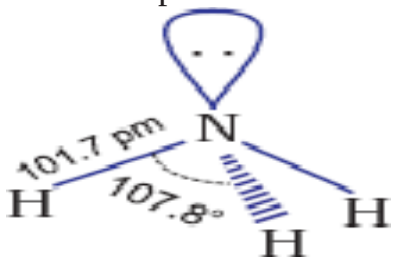
The p-Block Elements

Properties

Ammonia is a colourless gas with pungent smell. It is highly soluble in water because of its ability to form inter molecular hydrogen bond with water. Liquid ammonia has high melting and boiling points because of inter molecular hydrogen bonding.

The ammonia molecule has a *Trigonal pyramidal geometry*. It has three bond pairs and one lone pair of electrons.



Its aqueous solution is weakly basic due to the formation of OH^- ions.

$$NH_3(g) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$$

As a weak base, it precipitates the hydroxides of many metals from their salt solutions.
For example, $2FeCl_3(aq) + 3NH_4OH(aq) \rightarrow Fe_2O_3.xH_2O(s) + 3NH_4Cl(aq)$

$$ZnSO_4(aq) + 2NH_4OH(aq) \rightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$$

The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms complex compounds with Cu^{2+}, Ag^+ etc. So it is used for the detection of these metal ions.

$$\underset{\text{(blue)}}{Cu^{2+}(aq)} + 4\,NH_3(aq) \rightarrow \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}(aq)}$$

$$\underset{\text{(colourless)}}{Ag^+(aq)} + Cl^-(aq) \rightarrow \underset{\text{(white ppt)}}{AgCl(s)}$$

$$\underset{\text{(white ppt)}}{AgCl(s)} + 2NH_3(aq) \rightarrow \underset{\text{(colourless)}}{[Ag(NH_3)_2]Cl(aq)}$$

Uses: Ammonia is used

(i) to produce various nitrogenous fertilizers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate)

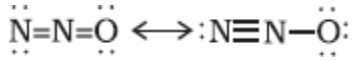
(ii) in the manufacture of nitric acid

(iii) liquid ammonia is used as a refrigerant.

Oxides of Nitrogen

Nitrogen forms a number of oxides in different oxidation states. They are:

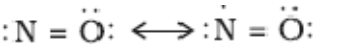
1. **Nitrous Oxide [Nitrogen (I) Oxide]**: It is prepared by heating ammonium nitrate. $NH_4NO_3 \rightarrow N_2O + 2\ H_2O$



It is a colourless, neutral gas. Its structure is:

2. **Nitric Oxide [Nitrogen (II) Oxide]**: It is prepared by treating sodium nitrite with acidified ferrous sulphate.

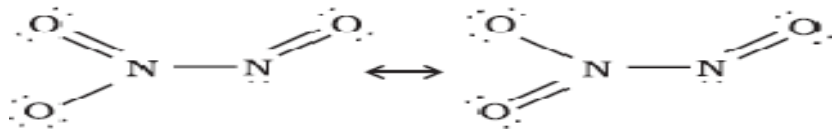
$$2\ NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$$



It is a colorless neutral gas. Its structure is:

3. **Dinitrogen trioxide [Nitrogen (III) oxide]**: It is prepared by treating nitric oxide with dinitrogen tetroxide It is a blue solid with acidic nature. Its structure is

$$2\ NO + N_2O_4 \xrightarrow{250K} 2\ N_2O_3$$



4. **Nitrogen dioxide [Nitrogen (IV) oxide]**: It is prepared by heating lead nitrate at about 673K.

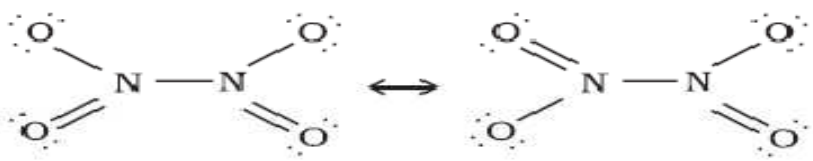
$$2Pb(NO_3)_2 \xrightarrow{673K} 4\ NO_2 + 2\ PbO + O_2$$

It is an acidic brown gas. Its structure is:

5. **Dinitrogen tetroxide [Nitrogen (IV) oxide]**: It is prepared by cooling NO_2.

$$2\ NO_2 \underset{\text{Heat}}{\overset{\text{cool}}{\rightleftharpoons}} N_2O_4$$

It is a colourless solid or liquid with acidic character. Its structure is:

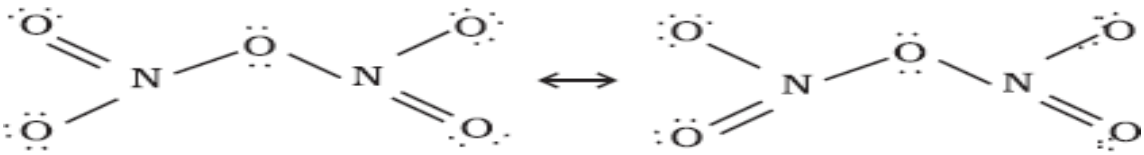


6. **Dinitrogen pentoxide [Nitrogen (V) oxide]**:

It is prepared by nitric acid with phosphorus pentoxide.

$$4\ HNO_3 + P_4O_{10} \rightarrow 4\ HPO_3 + 2\ N_2O_5$$

It is a colourless solid with acidic character. Its structure is:



Nitric Acid (HNO_3)

Preparation: In the laboratory, nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

On a large scale it is prepared by **Ostwald's process**. It involves three steps:

1.The catalytic oxidation of NH_3 by atmospheric oxygen in presence of platinum/ rhodium gauge (wire) catalyst.

$$4\ NH_3(g) + 5\ O_2(g) \xrightarrow{\text{Pt/Rh gauge catalyst, 500K \& 9 bar}} 4NO(g) + 6\ H_2O(g)$$

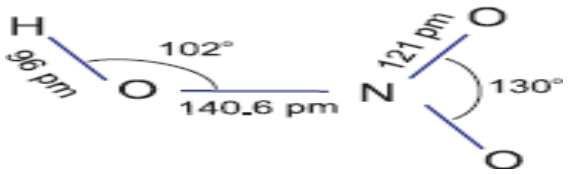
2.The nitric oxide is converted to NO_2 $\quad 2NO(g) + O_2(g) \longrightarrow 2\ NO_2\ (g)$

3.Absorption of nitrogen dioxide in water to get nitric acid.

$$3\ NO_2(g) + H_2O(l) \longrightarrow 2\ HNO_3(aq) + NO(g)$$

The aqueous HNO_3 can be concentrated by distillation up to 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4. 98% HNO_3 is known as *fuming nitric acid*.

Properties: It is a colourless liquid. In the gaseous state, HNO_3 exists as a planar molecule with the structure as shown below:



In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

$$3Cu + 8\ HNO_3(\text{dilute}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3(\text{conc.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Zinc reacts with dilute nitric acid to give N_2O and with concentrated acid to give NO_2.

$$4Zn + 10HNO_3(\text{dilute}) \rightarrow 4\ Zn\ (NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3(\text{conc.}) \rightarrow Zn\ (NO_3)_2 + 2H_2O + 2NO_2$$

Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Concentrated nitric acid also oxidizes non–metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to H_2SO_4, and phosphorus to phosphoric acid.

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

$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$$

$$S_8 + 48HNO_3(\text{conc.}) \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

$$P_4 + 20HNO_3(\text{conc.}) \rightarrow 4H_3PO_4 + 20\ NO_2 + 4H_2O$$

Brown Ring Test: It is a test used for the detection of nitrates. The test is carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicate the presence of nitrate ion in solution.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe\ (H_2O)_6]^{2+} + NO \rightarrow [Fe\ (H_2O)_5\ (NO)]^{2+} + H_2O$$

(brown ring)

Uses: It is used i) in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics. ii) for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds.iii) in the *pickling of stainless steel,* etching of metals and as an oxidiser in rocket fuels.

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