1. Details of Module and its Structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 03 (Class XII, Semester 01)
Module Name/Title	p-block Elements (Group 15 elements): Part 1
Module ID	lech_10701
Pre-requisites	Knowledge about electronic configuration of elements of this block and variation of Atomic size, Ionization Enthalpy, Electron Gain Enthalpy and Electronegativity within the groups in the block, chemical bonding
Objectives	After going through this module, the learners will be able to understand the following: 1. Anomalous behavior of nitrogen. **2.** Hydrides, oxides and halides of group 15 elements and their properties. **3.** Preparation and properties of dinitrogen. **4.** Preparation and properties of ammonia. **5.** Preparation and properties of nitric acid. **6.** Preparation and properties of oxides of nitrogen.
Keywords	Nitrogen, phosphorus, hydrides, halides, oxides, oxoacids, group 15.

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1. **Introduction-** The group 15 elements have general electronic configuration of ns^2np^3. They all have stable half filled electronic configuration. The group 15 elements are called pnictogens and their compounds as pnictides (As per IUPAC Recommendations available on https://www.iupac.org/fileadmin/user_upload/databases/Red_Book_2005.pdf). In this module we will discuss the general trends and the chemistry of nitrogen and phosphorus and their compounds. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a typical metal.

Phosphorus

Arsenic

Antimony

Bismuth

(Image source: https://en.wikipedia.org/wiki/)

<u>OCCURENCE</u>

The Earth’s atmosphere consists of 78% (by volume) molecular nitrogen. Nitrogen in much smaller amounts has also been discovered in the atmospheres of Venus and Mars. The atmosphere of Venus has 3.5% nitrogen by volume while that of Mars contains 2.7% nitrogen by volume. Nitrogen is the constituent of animal and plant proteins. Important nitrogen-containing minerals are KNO_3 (saltpeter, nitre), and $NaNO_3$ (Chile saltpeter, sodanitre), , which are found in arid regions and as growths on cave walls and ceilings. Both these salts are important components of fertilizers. Phosphorus occurs in minerals of the apatite family, $Ca_9(PO_4)_6$. CaX_2 (X = F, Cl or OH) (e.g., fluorapatite $Ca_9(PO_4)_6$. CaF_2) which are the main components of phosphate rocks. Phosphorus plays crucial roles in the biochemistry of all living things. It is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. Phosphorus is unique in the sense that it was first isolated in 1669 by Hennig Brandt from animal excreta (human urine) and later from plants before being found in minerals. Arsenic, antimony and bismuth are found mainly as sulphide minerals.

2. General properties of Group 15 elements

2.1 **Electronic Configuration**- The valence shell electronic configuration of these elements is ns^2np^3. They all have stable half- filled valence electronic configuration.

2.2 **Atomic and Ionic radii**- Atomic size increases down the group however, from As to Bi only a small increase in the covalent radius is observed. This is because from As to Bi, the addition of completely filled poor shielding inner d and/or f orbitals results in increase in the effective nuclear charge on the valence shell which opposes the increase in atomic radii.

2.3 **Ionization Enthalpy**- Ionization enthalpy of these elements decreases down the group due to increase in atomic size. First Ionization enthalpy of group 15 elements is much higher than those of the corresponding elements of group 14 due to the extra stability associated with half-filled p orbitals.

2.4 **Electronegativity**- In general electronegativity decreases down the group. For heavier members of the group however there is much less decrease in electronegativity.

2.5 **Physical state** - All the elements of this group are polyatomic. Nitrogen exists as a diatomic gas while P, As, Sb and Bi exist as solids. Except nitrogen, all the elements show allotropy.

2.6 **Metallic character** - Decrease in ionisation enthalpy down the group results in increased metallic character for heavier members. Nitrogen and phosphorus are non metals, arsenic and antimony are metalloids while Bi is a metal.

2.7 **Melting and boiling points** - The boiling points, in general, increase from top to bottom in the group but the melting point increases up to arsenic and then decreases up to bismuth.

2.8 **Oxidation states** - The common oxidation states of these elements are –3, +3 and +5.

The tendency to display negative oxidation state decreases down the group due to increased metallic character resulting from increasing atomic size. **The stability of +5 oxidation state decreases and that of +3 oxidation state increases down the group**. This is because of the increased effective nuclear charge on valence shell resulting from addition of poor shielding inner d and/or f orbitals in heavier members. This effect coupled with decreased bond energies for heavier members forces the ns^2 electron pair to exclude itself from bonding and remain inert. This will result in greater stabilisation of +3 oxidation state as compared to +5 oxidation state. This is also termed as **inert pair effect**. Bismuth being a metal, does not display -3 oxidation state and being the heaviest member of the group exhibits a stable +3 oxidation state in its compounds rather than +5 oxidation state. It exhibits + 5 oxidation state only when bonded to most electronegative element fluorine in BiF_5. Nitrogen also exhibits + 1, + 2, and + 4 oxidation states in its oxides and oxoacids. Phosphorus also shows +1 and +4 oxidation states in some oxoacids. In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution as they are intermediate oxidation state so can be oxidised or reduced further.

e.g., $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

Here in nitrous acid, N is in +3 oxidation state so on disproportionation it changes to +5 in nitric acid and +2 in nitric oxide. Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid.

$$4H_3PO_3 \rightarrow H_3PO_4 + PH_3$$

However +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.

2.9 **Anomalous behaviour of nitrogen –** Nitrogen being the lightest member of the group shows anomalous properties compared to other group 15 elements. This is due to small size, high ionization enthalpy, absence of d-orbitals and high electronegativity. Some of the anomalies observed are:

2.9.1 *Nitrogen exists as diatomic (N_2) gas*

This can be explained on the basis of unique tendency of nitrogen to form extremely stable pπ-pπ multiple bonds with itself (N ≡ N bond, bond enthalpy 941.4 KJ/mol) because of effective lateral overlap of small 2p atomic orbitals. The stable diatomic molecules so generated have only weak *van der waals forces between them and thus* exist in gaseous state. Nitrogen forms similar stable pπ - pπ multiple bonds with C and O also (C=N, C≡ N, N=O). The other group 15 elements owing to larger orbital size for *np* orbitals, donot give rise to an effective lateral orbital overlap and hence do not form stable pπ - pπ multiple bonds.

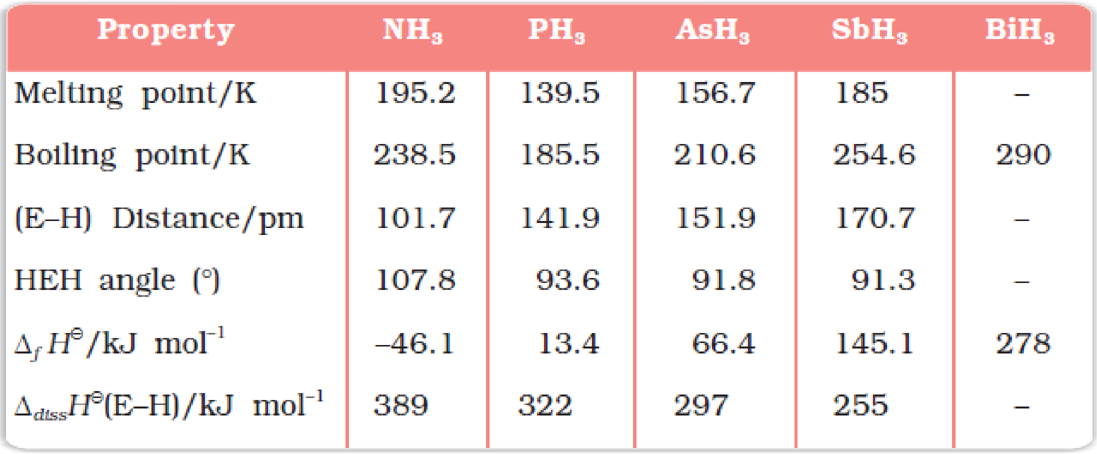
2.9.2 *Nitrogen lacks catenation tendency* because of the weakness of N-N single bond. This is attributed to the lone pair –lone pair repulsion between two bonded nitrogen atoms. The other elements however form stable single bond as their large size and hence longer bond length leads to reduced lone pair-lone pair repulsions between bonded atoms.

2.9.3 *Nitrogen can have a maximum covalency of four* only since total four valence orbitals (one 2*s* and three 2*p)* are available for bonding. The heavier elements have vacant *d* orbitals in the outermost shell (ns^2 np^3 nd^0) which can also be used for bonding and hence they can expand their covalency upto six as in $[PF_6]^-$. The d orbitals are further used by phosphorus and arsenic to form dπ - pπ multiple bonds with atoms like carbon, oxygen and nitrogen and dπ – dπ multiple bonds in complexes with transition elements and their compounds (PH_3, PR_3 etc. act as ligands for transition metals).

3. Hydrides of Group 15 elements

All elements (E) of group 15 form hydrides of common composition EH_3 . Some physical properties of these hydrides are enlisted in table 1.1 .

Table 1.1 PHYSICAL PROPERTIES OF HYDRIDES OF GROUP 15 ELEMENTS



Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point/K	195.2	139.5	156.7	185	–
Boiling point/K	238.5	185.5	210.6	254.6	290
(E–H) Distance/pm	101.7	141.9	151.9	170.7	–
HEH angle (°)	107.8	93.6	91.8	91.3	–
$\Delta_f H^\ominus$/kJ mol^{-1}	–46.1	13.4	66.4	145.1	278
$\Delta_{diss} H^\ominus$(E–H)/kJ mol^{-1}	389	322	297	255	–

3.1. Thermal stability

Thermal stability refers to stability towards decomposition on heating a compound. Thermal stability of these hydrides decreases down the group because as the size of the central atom increases down the group, E-H bond strength decreases.

3.2 Reducing power

These hydrides act as reducing agents. Reducing power of these hydrides increases in the order $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$. This is because stability of hydride decreases on moving down the group so E-H bond can be easily cleaved to supply hydrogen for reduction.

3.3 Lewis basicity

The presence of the lone pairs on central atom in these hydrides imparts lewis basicity to the compound. The basicity of these hydrides decreases down the group in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. The increasing orbital size of central atom down the group results in the decreased lone pair electron density on the central atom in EH_3 and hence reduced electron pair donor ability.

3.4 Bond Angle

Bond angle H-E-H decreases down the group $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$**..** The increase in size of central atom results in lone pair being present in larger hybridized orbitals. This leads to lone pair-bond pair dominating the bondpair - bond pair repulsions .

3.5 Boiling points

All these hydrides exist as gases at room temperature. The boiling points of these hydrides increase in the order $PH_3 < AsH_3 < SbH_3 < BiH_3$. The only force of attraction between the molecules of these hydrides is van der waals forces which increase with increasing size of the molecule. Ammonia has exceptionally high boiling point in the series. N-H bond polarity is very high which gives rise to stronger association of ammonia molecules due to intermolecular H-bonding.

4. Oxides of Group 15 Elements

Group 15 elements form primarily two types of oxides E_2O_3 and E_2O_5. The oxide in the higher oxidation state (+5) of the element is more acidic than that of lower oxidation state (+3). N_2O_5 is more acidic than N_2O_3.

For one type of oxide, the acidic character of these oxides decreases down the group with decreasing electronegativity of group 15 element. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony are amphoteric and that of bismuth is predominantly basic.

5. Halides of Group 15 elements

These elements form two series of halides: EX_3 and EX_5. **Nitrogen does not form any pentahalide due to non-availability of the *d* orbitals in its valence shell.** Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable because of high N-F bond strength. Trihalides except BiF_3 are predominantly covalent in nature. Bi being electropositive element and fluorine being the most electronegative element, bismuth trifluoride is predominantly ionic in nature.

NF_3 is remarkably unreactive compared to NCl_3 which undergoes a rapid hydrolysis. This difference lies in the low N-Cl bond strength and presence of vacant d orbitals in Cl atom. In contrast to nitrogen trihalides, phosphorus trihalides are quite reactive towards hydrolysis because of the presence of vacant d orbitals on P (This also explains why hydrolysis products are different for two types of halides).

$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$

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

6. Binary compounds of Group 15 elements with metals-

Group 15 elements react with metals to form binary compounds in which they display -3 oxidation state. These are calcium nitride (Ca_3N_2), calcium phosphide (Ca_3P_2), sodium arsenide (Na_3As), zinc antimonide (Zn_3Sb_2) and magnesium bismuthide (Mg_3Bi_2).

7. Dinitrogen (N_2)

7.1. Preparation

Dinitrogen (molecular nitrogen) is produced commercially by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.pt.90 K). In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$NH_4CI(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl\ (aq)$

Small amounts of NO and HNO_3 are also formed in the side reactions; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate. It can also be obtained by the thermal decomposition of ammonium dichromate.

$(NH_4)_2Cr_2O_7\ (s) \rightarrow N_2\ (g) + 4H_2O\ (l) + Cr_2O_3\ (s)$

High purity nitrogen can be obtained by the thermal decomposition of sodium azide at 573 K.

$2NaN_3 (s) \rightarrow 2Na (s) + 3N_2 (g)$

7.2 Properties

Dinitrogen is a colourless, odourless, tasteless and non-toxic gas. Nitrogen atom has two stable isotopes: ^{14}N and ^{15}N. **Dinitrogen is inert at room temperature because of the high bond enthalpy of N≡N bond (941.5 KJ/mol)**. At higher temperatures, it directly combines with highly electropositive metals like Li and alkaline earth metals to form predominantly ionic nitride and with of non-metals to form covalent nitrides.

$6Li (s) + N_2 (g) \rightarrow 2Li_3N (s)$

It combines with hydrogen at about 773 K in the presence of a catalyst (Haber Bosch Process) to form ammonia.

Dinitrogen combines with oxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

$N_2 (g) + O_2 (g) \rightarrow 2NO(g)$

7.3 Uses of dinitrogen

The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide). It also finds use where an inert atmosphere is required (e.g., in iron and steel industry, inert diluent for reactive chemicals). Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

8. Ammonia (NH_3)

8.1. Preparation

Ammonia is naturally present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea. On laboratory scale ammonia is prepared by treating ammonium salts with caustic soda or calcium hydroxide.

$(NH_4)_2SO_4 + 2NaOH (aq) \rightarrow 2NH_3 (g) + 2H_2O (l) + Na_2SO_4 (aq)$

$2NH_4Cl (s) + Ca(OH)_2 (aq) \rightarrow 2NH_3 (g) + 2H_2O (l) + CaCl_2 (aq)$

On industrial scale, ammonia is manufactured by **Haber Bosch** process (Fig.1.1) which involves direct reaction between nitrogen and hydrogen at high pressure (200-400 atm) at a temperature of ~ 700 K in presence of an iron catalyst. The catalyst iron oxide is mixed with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta Hf^0 = -46.1 \text{ kJ mol}^{-1}$$

As the reaction proceeds, there is a decrease in the number of gaseous molecules decreasing the overall pressure of the reaction mixture. In accordance with Le Chatelier's principle, high pressures are therefore required to shift the equilibrium in the favour of ammonia formation.

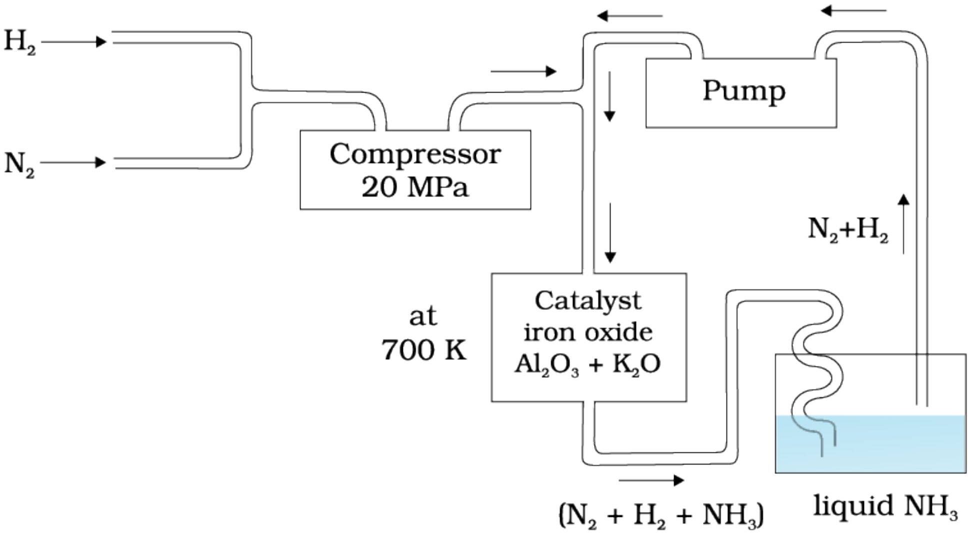


Fig.1.1. Synthesis of Ammonia by **Haber Bosch** process

8.2 Properties of Ammonia

Ammonia is a colourless gas with a pungent odour. Its freezing and boiling points are 195.4 and 239.7 K respectively. The melting and boiling points are higher than expected on the basis of its molecular mass due to strong intermolecular H bonding. Ammonia is soluble in water partly due to hydrogen bonding with water and partly due to hydrolysis. The ammonia molecule is trigonal pyramidal (Fig. 1.2) with lone pairs of nitrogen atom occupying one of the vertices. It has three bond pairs and one lone pair of electrons as shown in the structure.

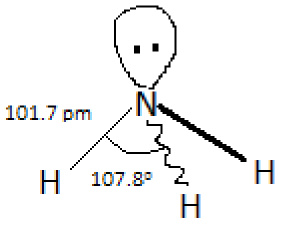


Fig. 1.2. Structure of Ammonia

Aqueous solution of ammonia is weakly basic because of the equilibrium

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

It forms ammonium salts on reacting with mineral acids, e.g., NH_4Cl, $(NH_4)_2SO_4$, etc.

$NH_3\ (g) + HCl\ (g) \rightarrow NH_4Cl\ (s)$

As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions.

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

White ppt.

$FeCl_3\ (aq) + 3NH_4OH\ (aq) \rightarrow Fe_2O_3.xH_2O\ (s) + 3\ NH_4Cl\ (aq)$

Brown ppt.

Ammonia in laboratory can be detected by Nesseler's reagent.

$2K_2[HgI_4] + NH_3 + 3KOH \rightarrow HgO.\ Hg(NH_2)I + 7\ KI + 2H_2O$

Nesseler's Reagent   Brown ppt.

Ammonia being a lewis base, donates its electron pair on nitrogen to transition metal ions to form a coordinate bond. The formation of such complex compounds finds applications in detection of metal ions such as Cu^{2+}, Ag^+ etc.

$Cu^{2+}\ (aq) + 4NH_3\ (aq) \rightarrow [Cu(NH_3)_4]^{2+}\ (aq)$

Blue   deep blue

$Ag^+\ (aq) + Cl^-\ (aq) \rightarrow AgCl\ (s)$

Colourless   White ppt

$AgCl\ (s) + 2NH_3\ (aq) \rightarrow [Ag(NH_3)_2]^+Cl^-\ (aq)$

White ppt soluble

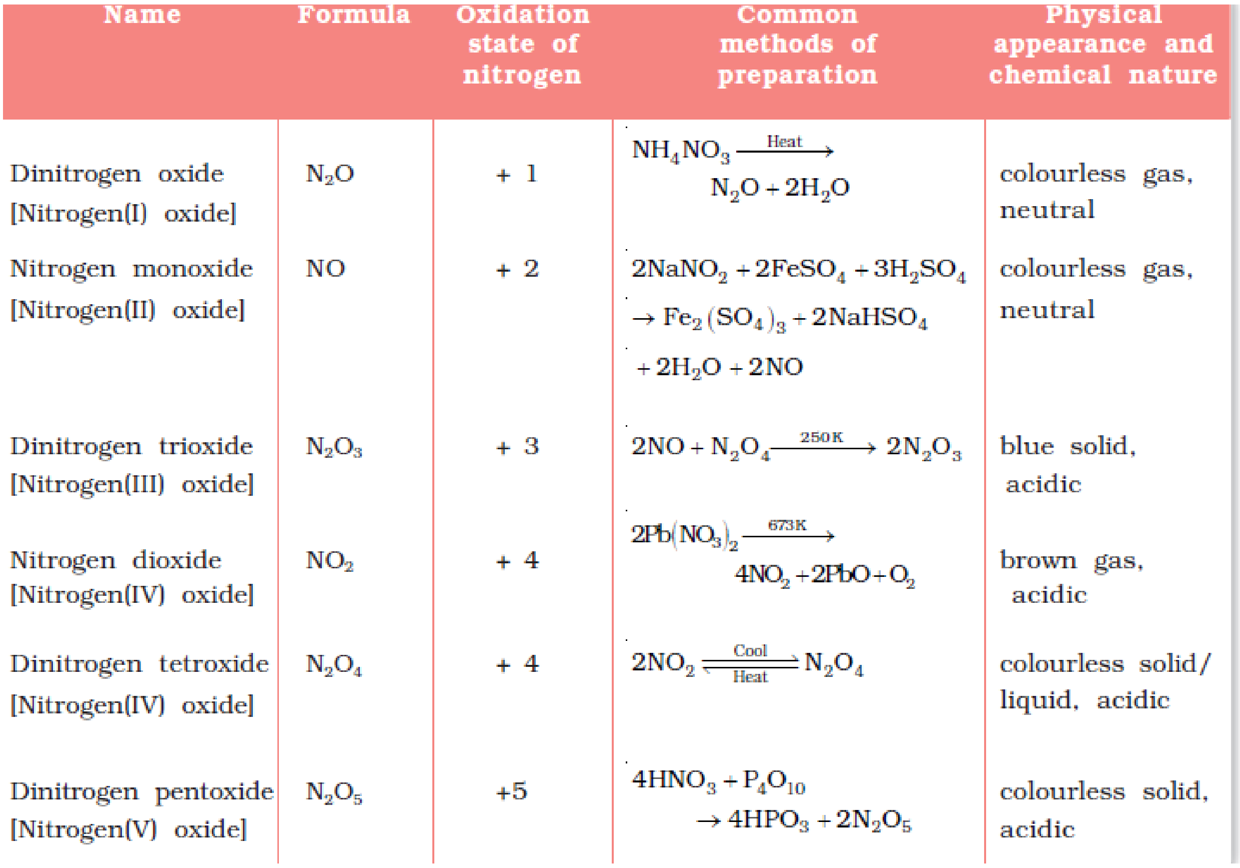
8.3 Uses of Ammonia

Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important being nitric acid. Liquid ammonia is also used as an environmentally friendly refrigerant. Liquid ammonia is used as a non aqueous solvent and is represented as $NH_3(l)$. It has unique property to dissolve alkali metals forming deep blue solutions with remarkable properties. The term liquor ammonia is used for aqueous solution of ammonia and is represented as $NH_3(aq)$.

9. Compounds of Nitrogen and oxygen.

9.1. Oxides of Nitrogen- Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table 1.2 below.

Table 1.2. Preparation , physical appearance and chemical nature of oxides of nitrogen



Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250\,K} 2N_2O_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic

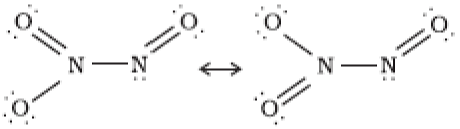
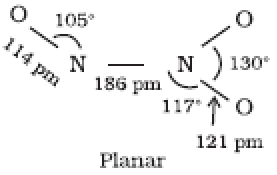
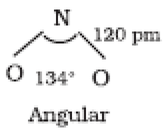
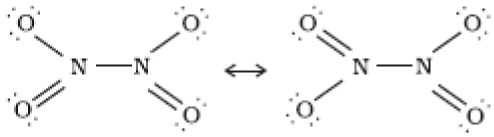
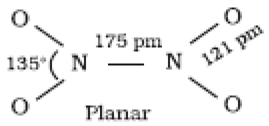
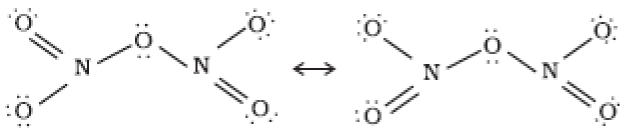
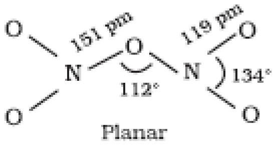
Both NO and NO_2 have odd number of electrons but only NO_2 forms stable dimer N_2O_4 which is colourless and diamagnetic.

$$2\,NO_2(g) \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4\,(l)$$

When N_2O_4 is heated the colour darkens and paramagnetic character increases due to its decomposition to monomeric NO_2.

The structures of these oxides are given in Table 1.3 below-

Table 1.3- Structure of oxides of nitrogen

Formula	Resonance Structures	Bond Parameters
N_2O	$\ddot{N}=N=\ddot{O} \longleftrightarrow :N\equiv N-\ddot{O}:$	N — N — O 113 pm 119 pm Linear
NO	$:N=\ddot{O}: \longleftrightarrow :\dot{N}=\ddot{O}:$	N — O 115 pm
N_2O_3		
NO_2		
N_2O_4		
N_2O_5		

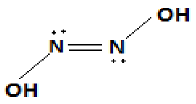
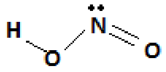
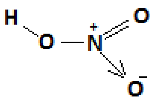
Nitrous oxide **N_2O** is a central nervous system depressant and asphyxiant and is used as a dental anesthetic. For this purpose it is mixed with oxygen and is administered through nose with a gas mask. It produces a tingling sensation in arms and legs at lower concentrations and is known as **laughing gas**. The response of body towards different concentrations of administered N_2O is variable.

Reference reading for NO: http://www.dentalfearcentral.org/help/sedation-dentistry/laughing-gas/

9.2. Oxoacids of Nitrogen

Nitrogen forms three oxoacids which are listed in Table 1.4. Amongst these nitric acid is the most important acid.

Table 1.4: Name, formula and structure of oxoacids of nitrogen

Name of Oxoacid	**Formula**	**Oxidation state of Nitrogen atom**	**Structure**
Hyponitrous acid	$H_2N_2O_2$	+1	
Nitrous acid	HNO_2	+3	
Nitric acid	HNO_3	+5	

9.2.1. Nitric Acid

9.2.1.1. *Preparation*

In the laboratory, nitric acid is prepared by heating $Ba(NO_3)_2$ with concentrated H_2SO_4. The insoluble barium sulphate is removed by filtration and the filtrate can be used as aqueous nitric acid.

$Ba(NO_3)_2$ (aq) + H_2SO_4 (conc.) → $BaSO_4$ (s)+ HNO_3(aq)

On industrial scale it is prepared mainly by Ostwald's process which uses catalytic oxidation of NH_3 by atmospheric oxygen. The various steps involved are:

1. Catalytic oxidation of ammonia to nitric oxide

Pt/Rh gauge catalyst

$4NH_3$ (g) + $5O_2$ 4NO (g) + $6H_2O$ (g)

(from air) 500 K, 9 bar

In primary oxidation 95 per cent of ammonia is converted into nitric oxide (NO).

2. Oxidation of nitric oxide to nitrogen dioxide by oxygen from air

$2NO (g) + O_{2\,(g)} \rightarrow 2\,NO_2 (g)$

3. Hydrolysis of nitrogen dioxide (disproportionation in water) to give nitric acid and nitric oxide

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

NO thus formed is recycled again in step 2. The aqueous nitric acid so obtained is dilute and can be concentrated by distillation to 68% (by mass). 98% concentration of nitric acid can be achieved by drying the moist nitric acid with concentrated sulphuric acid.

9.2.1.2. Properties of Nitric acid

Nitric acid is a colourless liquid (m.p. 231.4 K and b.p. 355.6 K). Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504. In the gaseous state, HNO_3 exists as a planar molecule with the structure as shown in Fig 1.3. In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

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

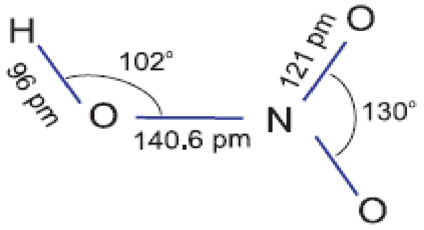


Fig 1.3. Structure of nitric acid

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.

$3Cu\ (s) + 8\ HNO_3\ (dil.) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

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

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

$4Zn + 10HNO_3\ (dil.) \rightarrow 4\ Zn\ (NO_3)_2 + 5H_2O + N_2O$

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

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 oxidises 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.

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

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

$S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$

$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

Identifying Nitrate in any salt : Brown Ring Test

It can be performed by adding freshly prepared ferrous sulphate solution to a solution of a nitrate salt, followed by addition of concentrated H_2SO_4 along the walls of the test tube taking care that it does not mix with the solution to be analysed for nitrate. Allow the acid to form a layer below the aqueous solution of nitrate. A brown ring (Fig 1.3) will form at the junction of the two layers, indicating the presence of the nitrate ion. The overall reaction is the reduction of the nitrate ion by iron(II) which is oxidised to iron(III) leading to the formation of a nitrosonium complex where nitric oxide is oxidised to NO^+.

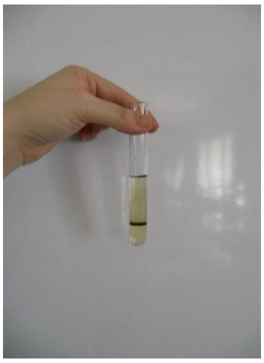


Fig 1.4. Brown ring formed at the junction

(Image source: https://en.wikipedia.org/wiki/Nitrate_test#/media/File:Brown_Ring_Test_in_Sam_Tet.jpg)

$2HNO_3$ (aq) + $3H_2SO_4$ (aq) + $6FeSO_4$ (aq) → $3Fe_2(SO_4)_3$ (aq) + 2NO (g) + $4H_2O$ (L)

$FeSO_4$ (aq) + $6H_2O$ (l) → $[Fe(H_2O)_6]SO_4$ (aq)

$[Fe(H_2O)_6]SO_4$ (aq) + NO (g) → $[Fe(H_2O)_5(NO)]SO_4$ (aq) + H_2O (l)

Brown ring species formed at junction

9.2.1.3. Uses of Nitric acid

The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics. Such as nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the *pickling of stainless steel*, etching of metals and as an oxidiser in rocket fuels.

10. Summary

Group 15 consists of five elements namely nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) which have general valence electronic configuration ns^2np^3. Small size of nitrogen atom with no d orbital in valence shell has considerable effect on its physical and chemical properties resulting in nitrogen showing anomalous behaviour from other elements of the group. This is reflected in extremely stable pπ-pπ multiple bonds involving nitrogen with itself and with other elements of second period like carbon and oxygen. Nitrogen displays a maximum covalency of four only.

Group 15 elements display two prominent stable oxidation states +3 and +5 though nitrogen displays all oxidation states from -3 to +5. Inert pair effect is well demonstrated by the group 15 elements with +3 oxidation state more stable for heavier elements. Nitrogen in its elemental form, dinitrogen (N_2) as well as its compounds like oxides, hydrides and oxoacid, find significant importance at laboratory and commercial scale. Its hydride, ammonia is synthesised using Haber Bosch’s process and nitric acid by Ostwald process. Nitrogen also forms a constituent element in living beings present in the form of proteins, nucleic acids and enzymes.