

# 1

CHAPTER

# GROUP 15 ELEMENTS



- \* General Characteristics
- \* Oxy Acids
- \* Hydrides, Halides and Oxides
- \* Ammonia and Nitric Acid

## GENERAL CHARACTERISTICS

### 1.1.1

#### Position in periodic table

Nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) are the five elements of group VA. They are located in the p-block of the long form of the periodic table. These elements are assigned group 15 by the I.U.P.A.C. These are called **elements of nitrogen family** or some times called elements of nitrogen-phosphorus family. These elements are named as **pnicogens**. Their position in the long form of the periodic table is indicated by shaded portion in Table 1.1.

Table 1.1 Position of group VA elements

IA	IIA											IIIA	IVA	VA	VIA	VIIA
		H										C	N	O		
												Si	P	S		
												Ge	As	Se		
												Sn	Sb	Te		
												Pb	Bi	Po		

*General electronic configuration of group 15 elements is  $ns^2np^3$*

Each of the group VA elements has five electrons in the valence shell. Two electrons are filled in the s-sub-shell and the remaining three in the p-sub-shell. The general electronic configuration of these elements is  $ns^2np^3$  and is given in the box method in Fig 1.1. Configurations are summarised in Table 1.2.

Electronic configuration in the ground state	$ns^2 np_x^1 np_y^1 np_z^1$ 
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Fig 1.1 Configuration of group VA elements

Table 1.2 Atomic numbers and electronic configuration of group VA elements

Element	Symbol	Atomic number	Configuration
Nitrogen	N	7	[He] 2s <sup>2</sup> 2p <sup>3</sup>
Phosphorus	P	15	[Ne] 3s <sup>2</sup> 3p <sup>3</sup>
Arsenic	As	33	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>
Antimony	Sb	51	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>
Bismuth	Bi	83	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>

In accordance with the Hund's rule of maximum spin multiplicity, the three electrons are distributed equally in the p-sub-shell. Thus these elements have **half-filled orbitals**. Due to the orbital symmetry, elements with exactly half filled orbitals are stable. Hence, the group VA elements are not so reactive and fairly stable.

Only two electrons are present in the penultimate shell of nitrogen, eight electrons in phosphorus and eighteen each in arsenic, antimony and bismuth. This shows why nitrogen differs in some of its properties from phosphorus and these two elements differ in their properties from the remaining elements of the group.

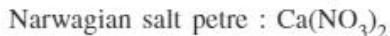
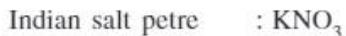
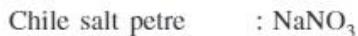
### 1.1.2

#### Occurrence

**Nitrogen occurs naturally as nitrate**

**Phosphorus occurs naturally as phosphate**

Nitrogen occurs even in free state, in air as dinitrogen, to the extent of 78% by volume and 75% by weight. In combined state, it exists as nitrate.



Most abundant element of group VA in the earth's crust is phosphorus. Its relative abundance in the earth's crust is 11.2 ppm. It is the eleventh most abundant element. The important source of phosphorus is phosphorite rocks which is mainly calcium phosphate. The same chemical form is also present in bones and teeth. Phosphoproteins are present in egg and milk.



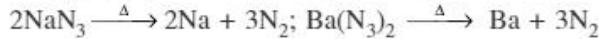
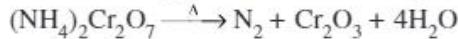
Arsenic, antimony and bismuth are available mainly as sulphide minerals.

Dinitrogen (N<sub>2</sub>) is commercially prepared by the fractional distillation of liquid air. Liquid nitrogen distils at 77K. In the laboratory, nitrogen is obtained by treating aqueous ammonium chloride solution with potassium nitrite.



The possible impurities, NO and HNO<sub>3</sub> are removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

Nitrogen can be obtained by heating ammonium dichromate. Pure nitrogen can be obtained by the thermal decomposition of azide.

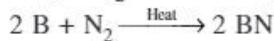


Dinitrogen is a colourless non-toxic gas. It is very less soluble in water.

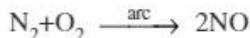
  
Nitrogen is chemically inert due to high bond enthalpy

  
inert due to high bond enthalpy

Dinitrogen is chemically inert at room temperature because of high bond enthalpy. At high temperature, nitrogen directly combines to give ionic nitrides with some metals and covalent nitrides with non-metals.



At about  $2000^\circ\text{C}$  (also during lightenings), nitrogen combines with oxygen to form nitric oxide.



Dinitrogen is used in the manufacture of ammonia, calcium cyanamide, etc. It is used as inert diluent for reactive chemicals and to create inert atmosphere. Liquid nitrogen is used as refrigerant and is cryosurgery

Phosphorus is prepared by the reduction of phosphate with coke and silica.



### 1.1.3

#### General properties

  
Nitrogen is a gas.  
Other elements of group 15 are solids



The similarities and gradation in the general physical properties of the group VA elements are summarised in Table 1.3.

**Atomic radius :** From nitrogen to bismuth, the atomic number and the atomic weight gradually increase. The differentiating electron enters in the next higher energy shell, suggesting an increase in the atomic radius. However, the increase in the radius is less predominant beyond phosphorus. This is due to the shielding effect by inner d-orbitals.

**Physical state :** Nitrogen is a gas at room temperature. Other elements of the group VA are solids. The melting and boiling points gradually increase from nitrogen to antimony. The smaller values of bismuth are attributed to a different crystal structure.

Table 1.3 Gradation in the physical constants of group VA elements

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic Weight	14.01	30.97	74.92	121.75	208.98
Covalent radius ( $\text{\AA}$ )	0.72	1.10	1.21	1.41	1.49
Density in solid state ( $\text{g cc}^{-1}$ )	0.88*	1.82	5.78	6.69	9.79
Melting point ( $^\circ\text{C}$ )	-210	44	816**	630	271
Boiling point ( $^\circ\text{C}$ )	-196	281	615	1587	1564
Ionisation potential ( $\text{kJ mol}^{-1}$ )	1402	1012	947	834	703
Electronegativity (Pauling scale)	3.0	2.1	2.0	1.9	1.9
M-M bond energy ( $\text{kJ mol}^{-1}$ )	355.5	200.7	163.1	146.4	-
Common oxidation states	-3, +3, +5	+3, +5	+3, +5	+3, +5	+3

\* Gas at room temperature

\*\* At 38 atm

  
**N and P are non-metals, but Bi is a metal**  


  
**Nitrogen is diatomic molecule with a triple bond**  
  
**Phosphorus is tetra-atomic molecule with tetrahedral structure**  


**Metallic nature :** The values of Pauling's electronegativity gradually decreases from nitrogen to bismuth. The metallic nature increases gradually with an increase in the atomic size. Nitrogen and phosphorus are non-metals. Arsenic and antimony are metalloids. A metalloid is the element which exhibits both metallic and non-metallic properties. Bismuth is clearly a metal of the group VA.

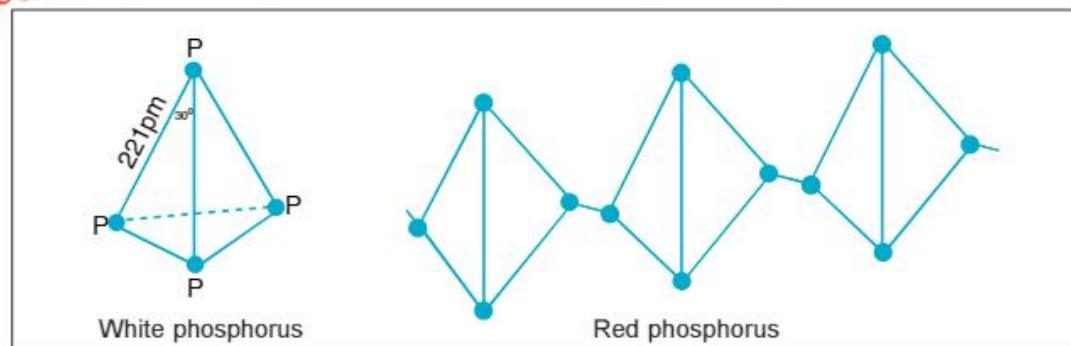
**Ionisation potential :** The ionisation potential values decrease gradually on descending the group as the atomic number increases. These values are relatively high compared to the corresponding elements of adjacent groups.

High ionisation value is attributed to the stable half-filled electronic configuration in the p sub-shells of these elements. The difference in the ionisation potential values after phosphorus is less predominant, which is attributed to shielding effect by inner d-orbitals.

**Atomicity :** Nitrogen is a diatomic molecule with a **triple bond** between two bonded atoms. The triple bond contains one sigma and two pi-bonds, with a bond energy of  $946 \text{ kJ mol}^{-1}$ . The bond is very strong, difficult to dissociate and hence is responsible for the **chemical inertness of nitrogen**.

Atomicity of phosphorus, arsenic and antimony is 4 each. They form tetra-atomic molecules, with four atoms occupying each corner of a regular tetrahedron as shown in Fig 1.2.

In the tetrahedral structure of phosphorus molecule, each phosphorus atom forms three covalent bonds with a P-P bond order equal to one and a total of six sigma bonds per molecule. The P-P bond length is 221 pm.



**Fig 1.2 Structures of white and red phosphorus molecules**

**Catenation :** The first three elements of the group VA exhibit catenation, but this property is much less than that of carbon of group IVA and sulphur of group VIA. Bond energy of N-N is less than that of P-P due to strong interelectronic repulsions (l.p-l.p) in N-N. Hence catenation power of nitrogen is less than that of phosphorus. From phosphorous to antimony catenation power decreases. This decrease is attributed to decrease in M-M bond energies.

**Allotropy :** The existence of an element in two or more forms of same physical state is called allotropy. All except bismuth of the group VA elements exhibit allotropy. In solid state, nitrogen has two allotropes,  $\alpha$ - and  $\beta$ -nitrogens. Nitrogen gas has no allotropes.

**Important allotropes of phosphorus are white, red and black**

**White phosphorus is stored under water**

**Nitrogen cannot form five bonds due to lack of valence d-orbitals**

Phosphorus has three important allotropes, white (or yellow), red and black. Other more doubtful allotropes like violet phosphorus and scarlet phosphorus are also reported.

White phosphorus is a colourless waxy translucent solid. It is poisonous and glows in dark due to chemiluminescence. It is insoluble in water but soluble in non polar organic solvents such as carbon disulphide. It undergoes disproportion on boiling with aqueous caustic soda, liberating phosphine.

White phosphorus is less stable, because of angular strain in its molecule at  $60^{\circ}$ . It catches fire readily in air to give dense white fumes of phosphorus pentoxide. For this reason of high reactivity in solid phase, it is stored under water.



Phosphorus dissolves in boiling caustic soda solution in an inert atmosphere giving phosphine gas



Red phosphorus is obtained by heating white phosphorus of  $573\text{ K}$  in inert atmosphere for about 3 days. Red phosphorus has iron grey lustre. It is non-poisonous and odourless. It is insoluble in water as well as in organic solvents. Red phosphorus is less reactive and does not glow in dark. Lower reactivity of red phosphorus is due to its polymeric chain structure.

Black phosphorus has two forms  $\alpha$ -black and  $\beta$ -black.  $\alpha$ -Black phosphorus is formed when red phosphorus is heated in a sealed tube at  $803\text{ K}$  for several days. It is stable, not oxidised in air, but can be sublimed in air. It has opaque monochinic or rhombohedral structure.  $\beta$ -Black phosphorus is prepared under high pressure, by heating white phosphorus at  $473\text{ K}$ . It is also stable in air and does not burn upto  $673\text{ K}$ . This is thermodynamically the most stable allotrope of phosphorus. Hence it is the standard state of phosphorus. It has layers like structure and it is good conductor of electricity.

Arsenic has three allotropic forms, grey (metallic), black and yellow (non-metallic). Similarly, antimony also has three allotropic forms, crystalline metallic, non metallic and explosive.

**Bonding and valency :** Each element of the group VA has five valence electrons and requires three more for attaining stable octet configuration. Thus the usual valency of these elements is 3. The maximum valency, however, is the group number 5.

Nitrogen cannot be pentavalent in its compounds due to lack of valence d-orbitals. The excitation of electron from  $2s$  to  $3s$  orbital is difficult in nitrogen, as the energy gap is high between L and M shells. In ammonium salts, the maximum covalency of nitrogen is four with three covalent bonds and one dative bond.

Due to its small size and high electronegativity, nitrogen can form ionic compounds with metals. By gaining 3 electrons, it forms metal nitrides, like  $Li_3N$ , and  $AlN$ . Phosphorus also has the tendency of forming metal phosphides. The heavier elements of group VA, have vacant valence d-orbitals. These orbitals can be used for covalency and expand their valency upto even 6, as in  $PF_6^-$ .

*Element that exhibits maximum number of oxidation states is nitrogen*

**Oxidation states :** The general oxidation numbers of the group VA elements are  $-3$ ,  $+3$  and  $+5$ . The negative oxidation state ( $-3$ ), is more predominant for nitrogen, due to its higher electronegativity and non-metallic nature.

Nitrogen exhibits maximum number of types of oxidation states in its compounds. These oxidation states are listed in **Table 1.4**. All oxidation states of nitrogen from  $+1$  to  $+4$  tend to disproportionate in acid solution.



**Table 1.4 Oxidation states of nitrogen**

S.No.	Name of the compound	Formula of the compound	Oxidation state of Nitrogen
1.	Ammonia	$\text{NH}_3$	$-3$
2.	Hydrazine	$\text{N}_2\text{H}_4$	$-2$
3.	Hydroxylamine	$\text{NH}_2\text{OH}$	$-1$
4.	Hydrazoic acid	$\text{N}_3\text{H}$	$-1/3$
5.	Ammonium nitrite	$\text{NH}_4\text{NO}_2$	$0$
6.	Nitrous oxide	$\text{N}_2\text{O}$	$+1$
7.	Nitric oxide	$\text{NO}$	$+2$
8.	Nitrous acid	$\text{HNO}_2$	$+3$
9.	Nitrogen dioxide	$\text{NO}_2$	$+4$
10.	Nitric acid	$\text{HNO}_3$	$+5$

*Due to inert pair effect,  $+3$  state is more stable than  $+5$  for bismuth*

In case of phosphorus all intermediate oxidation states disproportionate into  $-3$  and  $+5$ , both in acid as well as in alkali.

The importance of  $-3$  oxidation state decreases from nitrogen to phosphorus and then almost vanishes for bismuth. The  $+3$  state becomes increasingly stable for arsenic, antimony and bismuth. The tendency of exhibiting  $+5$  oxidation state by the group VA elements decreases from nitrogen to bismuth. This is because of the non-involvement of s-electron pair in bonding, called **inert pair effect**. Due to the inert pair effect,  $+3$  oxidation state is more stable for bismuth than  $+5$  state. Bismuth exhibits stable  $+5$  state in  $\text{BiF}_5$ .

All the elements of group 15 react with metals to form their binary compounds such as  $\text{Ca}_3\text{Al}_2$ ,  $\text{Ca}_3\text{P}_2$ ,  $\text{Na}_3\text{As}_2$ ,  $\text{Nn}_3\text{Sb}_2$ ,  $\text{Mg}_3\text{Bi}_2$ , etc, containing  $-3$  oxidation state.



**P.1.1**  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CN}^-$  and  $\text{NO}^+$  are isoelectronic but the former is chemically inert and later three are very reactive, why?

**Solution** Although each of the above has same electronic distribution in bonding orbitals, nitrogen is inert because of non-polar nature of bond and high  $\text{N} = \text{N}$  dissociation energy. Rest all ( $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{NO}^+$ ) are polar.



**P.1.2** The tendency to exhibit  $-3$  oxidation state by a group VA element decreases down. Why?

**Solution** Nitrogen exhibits  $-3$  state in nitride and phosphorus exhibits  $-3$  state in phosphide. Going down the group, the atomic size increases and metallic character also increases. Hence, the tendency to exhibit negative oxidation state decreases down the group VA.



**P.1.3** Write the following for a white phosphorus molecule : (a) oxidation state of P, (b) valency of P, (c) total number of bonds and (d) bond order.

**Solution** Oxidation state of phosphorus in  $P_4$  molecule is zero.

Valecy of P in  $P_4$  molecule is three. Each P atom forms 3 bond pairs and possesses one lone pair. Total number of P-P sigma bonds in a molecule of phosphorus is six.

Phosphorus-phosphorus bond order in  $P_4$  molecule is one.



**P.1.4** Nitrogen forms a simple diatomic molecule but other elements of same group do not form. Explain.

**Solution** Atomic size of nitrogen is very less. Hence 'N' atom can approach close to another 'N' atom. This facilitates the lateral overlap of the p-orbitals forming  $\pi$ -bonds.

Due to large size, other atoms of the same group form only single bonds, but not multiple bonds.



**P.1.5** White phosphorus is very reactive, but not the red one. Why?

**Solution** White phosphorus is very reactive, due to the P-P-P bond angle strain at  $60^\circ$ .

Red phosphorus is very stable, due to chain like polymeric structure.



**P.1.6** Maximum covalency of nitrogen is four. Explain.

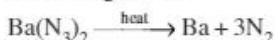
**Solution** Nitrogen has no valence d-orbitals. Excitation of 2s electron to 3s orbital is difficult. Hence nitrogen does not form five bonds.  $N(Z = 7) : [He] 2s^2 2p^1 2p^1 2p^1$

Nitrogen can form three covalent bonds and one dative bond as in  $NH_4^+$  or in  $C_6H_5NH_3^+$  ions. Its maximum covalency is four.



**P.1.7** What happens when barium azide is heated?

**Solution** Barium azide on heating undergoes thermal decomposition. Pure dinitrogen gas is obtained on heating azide.



**P.1.8** Phosphorus can expand its valency. Why?

**Solution** In its valency shell, phosphorus has vacant d-orbitals, which can be used for bonding. Hence, phosphorus can expand its valency upto 6, as in  $PF_6^-$ .

### EXERCISE - 1.1.1

1. Discuss on the electronic configuration of elements of group 15.
2. Mention the occurrence of nitrogen and phosphorus in the earth's crust.
3. Write the trends in atomic radius, metallic nature and ionisation potential of group VA elements.
4. Mention the oxidation numbers of the elements of nitrogen family in their compounds. Write suitable examples.
5. Discuss the bonding and valency of elements of group 15.
6. Write on the allotropy of group 15 elements.

## HYDRIDES, OXIDES AND HALIDES

### 1.2.1

#### Hydrides

The binary compounds formed by an element with hydrogen are called hydrides. All the elements of nitrogen family form the hydrides of the type  $MH_3$ , where M is the group VA element. The hydrides along with their characteristics are listed in Table 1.5.

Table 1.5 Hydrides of the group VA and their bond characteristics

Chemical formula	Name of the hydride	Boiling point	Heat of formation, kJ mol <sup>-1</sup>	H–M–H Bond angle	M–H bond energy kJ mol <sup>-1</sup>	M–H bond length, Å <sup>0</sup>
NH <sub>3</sub>	Ammonia	-34.5°C	-46.1	107°	389	1.017
PH <sub>3</sub>	Phosphine	-87.5°C	13.4	93°	321	1.419
AsH <sub>3</sub>	Arsine	-62.4°C	66.4	92°	297	1.519
SbH <sub>3</sub>	Stibine	-18.4°C	145.1	91°	255	1.707
BiH <sub>3</sub>	Bismuthine	17.0°C	277.9	91°	-	1.902

  
Ammonia is more stable among MH<sub>3</sub> type hydrides  


The M–H bond length increases and bond energy decreases from NH<sub>3</sub> to BiH<sub>3</sub>. Ammonia is the most stable. The stability gradually decreases from NH<sub>3</sub> to BiH<sub>3</sub>. In the same order of reactivity, the reduction ability increases down the group.

The central atom of these hydrides has a lone pair of electrons. According to Lewis theory of acids and bases, these hydrides act as bases. Ammonium salts are known, but phosphonium salts are less common. Ammonia is a weak base. Basic nature of these hydrides decreases from NH<sub>3</sub> to SbH<sub>3</sub>. BiH<sub>3</sub>, a metal hydride, does not exhibit the basic nature.

These hydrides form dative bonds, as they act as electron pair donors. The ability to donate electron pairs and form complex compounds decreases from NH<sub>3</sub> to BiH<sub>3</sub>.



These hydrides are all good reducing agents, except ammonia. The reduction ability increases with increase in the instability of the hydride.

Ammonia is the most soluble gas in water, as ammonia forms intermolecular hydrogen bonds with water. Moreover both ammonia and water are polar molecules. With a decrease in the electronegativity of the central atom in MH<sub>3</sub>, the polarity of M–H bond decreases and solubility in water also decreases.

Ammonia is prepared in the laboratory by the action of caustic soda on an ammonium salt. Metal phosphides upon hydrolysis give phosphine. Similarly metal arsenide or antimonide upon hydrolysis gives arsine or stibine.



All these hydrides are colourless, highly volatile, foul smelling and poisonous gases. Their ease of formation and the ease of substitution with groups like -Cl, -CH<sub>3</sub>, etc., decreases from ammonia to bismuthine.

The bond angle in NH<sub>3</sub> is nearer to tetrahedral angle and in the other hydrides of the group VA it is nearer to 90°. This is due to the use of sp<sup>3</sup> hybridised orbitals by the central atom in NH<sub>3</sub> and unhybridised p-orbitals by the central atoms of the other hydrides. The decrease in the bond angle from ammonia to phosphine is due to an increase in the size of the central atom and a decrease in the electronegativity of the central atom.

  
Ammonia is the most soluble gas in water  


  
From NH<sub>3</sub> to SbH<sub>3</sub>, bond energy and bond angle decrease  


  
**Reactivity and reduction ability increase from  $NH_3$  to  $SbH_3$**   


Ammonia can be liquified easily. Its volatility is less. Melting and boiling points of ammonia are higher than the expected values. This is due to intermolecular hydrogen bonding in ammonia.

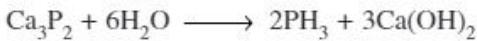
The order of volatility is :  $PH_3 > AsH_3 > NH_3 > SbH_3$

The order of basic nature is :  $NH_3 > PH_3 > AsH_3 > SbH_3$

The order of stability is :  $NH_3 > PH_3 > AsH_3 > SbH_3$

Besides these  $MH_3$  type hydrides, nitrogen forms other hydrides like hydrazine ( $N_2H_4$ ) and hydrazoic acid ( $N_3H$ ). Phosphorus is also known to form diphosphine ( $P_2H_4$ ) and tetraphosphine( $P_4H_6$ ) Diphosphine is neutral and has no action on litmus.

Phosphine is prepared by the reaction of calcium phosphide with water or dilute hydrochloric acid. In laboratory, phosphine is obtained by the action of concentrated caustic soda on hot white phosphorus, in carbondioxide atmosphere.



Pure  $PH_3$  is non-inflammable. The impurities present in phosphine are generally  $P_2H_4$  and vapours of  $P_4$ . Due to these impurities it becomes inflammable. Phosphine is absorbed in HI to form phosphonium iodide, which on treating with KOH gives off pure phosphine.



Phosphine is colourless and has the rotten fish odour. It is slightly soluble in water and aqueous solution decomposes in light giving red phosphorus.

Phosphine is a weak base. It forms phosphonium ions in acids, but it has no action on red litmus.



When phosphine is absorbed in solutions of metal salts, the corresponding phosphides are formed.



Phosphine is used in Holme's signals and also in smoke screens.

### 1.2.2

#### Oxides

  
 **$N_2O$  and  $NO$  are neutral oxides, but  $N_2O_5$  is more acidic**  


The binary compounds formed by an element with oxygen are called oxides. Nitrogen forms many oxides, because  $p\pi - p\pi$  bonds between nitrogen and oxygen are relatively stronger. These oxides, their common preparation methods and their nature are listed in Table 1.6.

Non-metallic oxides are usually acidic. However, nitrous oxide and nitric oxide are neutral oxides. With an increase in the oxidation number of nitrogen, the acidic nature of the oxide increases. Nitrogen pentoxide is most acidic among oxides of nitrogen.

Table 1.6 Oxides of nitrogen

Name of the oxide	Formula	Oxidation state of nitrogen	Common method of preparation	Physical appearance and chemical nature
Dinitrogen monoxide [Nitrogen(I) oxide]	N <sub>2</sub> O	+ 1	$\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$ $4\text{NH}_3 + 5\text{O}_2 \xrightarrow[\text{Pt, Heat}]{\quad} 4\text{NO} + 6\text{H}_2\text{O}$	Colourless gas, neutral
Dinitrogen trioxide Nitrogen (III) dioxide	N <sub>2</sub> O <sub>3</sub>	+3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_3$	Blue solid, acidic
Nitrogen dioxide [Nitrogen (IV) oxide]	NO <sub>2</sub>	+4	$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$	Brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N <sub>2</sub> O <sub>4</sub>	+4	$2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{N}_2\text{O}_4$	Colourless solid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N <sub>2</sub> O <sub>5</sub>	+5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	Colourless solid, acidic

Nitrous oxide is called laughing gas. It is a linear molecule. NO is colourless and is oxidised in the atmosphere to NO<sub>2</sub>. Nitric oxide is absorbed in freshly prepared ferrous sulphate to form a brown coloured complex,  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ , called brown ring.

The familiar brown ring test for nitrates depends on the ability of Fe<sup>2+</sup> to reduce nitrates to nitric oxide and nitric oxide react with ferrous to form brown complex.

N<sub>2</sub>O<sub>4</sub> is a dimer of NO<sub>2</sub>. NO<sub>2</sub> has one unpaired electron. It is brownish yellow and paramagnetic. But due to absence of unpaired electrons, N<sub>2</sub>O<sub>4</sub> is diamagnetic and colourless.

The group VA elements form two important types of oxides : trioxides with the general formula M<sub>2</sub>O<sub>3</sub> and pentoxides with the general formula M<sub>2</sub>O<sub>5</sub>. The oxides of phosphorus, arsenic and antimony exist as dimers (Table 1.7).

Table 1.7 Oxides of the group VA elements

Element	Trioxide	Pentoxide
Nitrogen	N <sub>2</sub> O <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>
Phosphorus	P <sub>4</sub> O <sub>6</sub>	P <sub>4</sub> O <sub>10</sub>
Arsenic	As <sub>4</sub> O <sub>6</sub>	As <sub>4</sub> O <sub>10</sub>
Antimony	Sb <sub>4</sub> O <sub>6</sub>	Sb <sub>4</sub> O <sub>10</sub>
Bismuth	Bi <sub>2</sub> O <sub>3</sub>	-

All these oxides are generally covalent and acidic. Sb<sub>4</sub>O<sub>6</sub> is amphoteric and Bi<sub>2</sub>O<sub>3</sub> is basic. Acidic nature decreases from the oxide of nitrogen to that of bismuth. Pentoxides are more acidic than the corresponding trioxides.

*NO<sub>2</sub> is paramagnetic, but N<sub>2</sub>O<sub>4</sub> is diamagnetic*

*Sb<sub>4</sub>O<sub>6</sub> is amphoteric and Bi<sub>2</sub>O<sub>3</sub> is basic*

Tri and pentoxides of nitrogen and phosphorus are important. Phosphorus pentoxide is a powerful dehydrating agent. The structures of the oxides of nitrogen are given in Fig 1.3 and those of phosphorus in Fig 1.4.

$\text{N}_2\text{O}$		$\text{N}=\text{N}-\ddot{\text{O}}$ $\ddot{\text{N}}=\text{N}-\ddot{\text{O}}:$	$\text{N}=\text{N}-\ddot{\text{O}}$ 113 pm $\ddot{\text{N}}=\text{N}-\ddot{\text{O}}:$ 110 pm Linear
$\text{NO}$		$:\ddot{\text{N}}=\ddot{\text{O}}:$ $:\ddot{\text{N}}=\ddot{\text{O}}:$	$\text{N}-\ddot{\text{O}}$ 115 pm
$\text{N}_2\text{O}_3$		$\text{N}_2\text{O}_3$ (Symmetric form)	$\text{O}=105^0$ $\text{N} 120 \text{ pm}$ $\text{N} 114 \text{ pm}$ $\text{O} 130^0$ $\text{O} 121 \text{ pm}$ Planar
$\text{NO}_2$		$:\ddot{\text{O}}=\ddot{\text{N}}-\ddot{\text{O}}:$ $:\ddot{\text{O}}=\ddot{\text{N}}-\ddot{\text{O}}:$	$\text{N} 120 \text{ pm}$ $\text{O} 134^0$ Angular
$\text{N}_2\text{O}_4$		$\text{N}_2\text{O}_4$	$\text{O} 135^0$ $\text{N} 175 \text{ pm}$ $\text{N} 121 \text{ pm}$ Planar
$\text{N}_2\text{O}_5$		$\text{N}_2\text{O}_5$	$\text{O} 151 \text{ pm}$ $\text{N} 112^0$ $\text{N} 119 \text{ pm}$ $\text{O} 134 \text{ pm}$ Planar

Fig 1.3 Structures of oxides of nitrogen

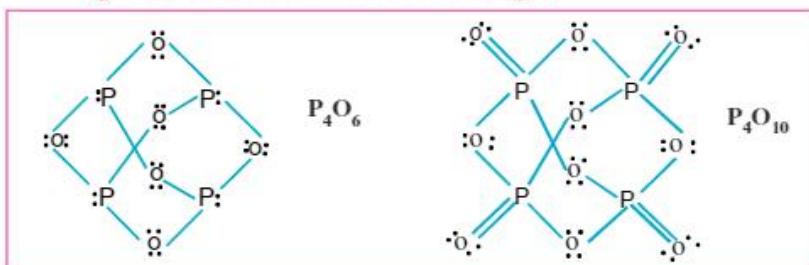
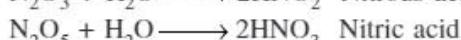
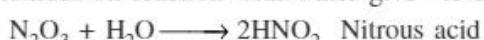


Fig 1.4 Structures of oxides of phosphorus

Number of 'O' atoms around 'P' atom in  $\text{P}_4\text{O}_6$  is 3 and in  $\text{P}_4\text{O}_{10}$  is 4

While  $\text{N}_2\text{O}_3$  and  $\text{P}_4\text{O}_6$  have only covalent bonds,  $\text{N}_2\text{O}_5$  and  $\text{P}_4\text{O}_{10}$  have covalent and co-ordinate covalent bonds. The number of oxygen atoms present around N atom in  $\text{N}_2\text{O}_3$  is 2 and in  $\text{N}_2\text{O}_5$  is 3 and around P atom in  $\text{P}_4\text{O}_6$  is 3 and in  $\text{P}_4\text{O}_{10}$  is 4. In solid phase  $\text{N}_2\text{O}_5$  exists as ionic compound, nitronium nitrate  $\text{NO}_2^+\text{NO}_3^-$ .

Trioxides on reaction with water give the corresponding -ous acids. Similarly pentoxides on reaction with water give -ic acids.



## 1.2.3

**Halides**

*Most stable halide of nitrogen is  $NF_3$*

The binary compounds formed by an element with halogen are called halides. The elements of nitrogen family form two types of halides. Trihalides with the formula  $MX_3$  have the oxidation number of the group VA element (M) +3. Pentahalides with the formula  $MX_5$  have the oxidation number of the group VA element +5.

Nitrogen does not form pentahalides, due to the lack of valence d-orbitals. The important and most stable halide of nitrogen is nitrogen trifluoride,  $NF_3$ . Nitrogen trichloride is yellow liquid and explosive.

Phosphorus, arsenic and antimony form pentahalides by using available d-orbitals in their excited states (Fig 1.5).

Ground state configuration	$ns^2$	$np^3$	$nd^0$
Excited state configuration	$ns^1$	$np^3$	$nd^1$

**Fig 1.5 Electronic configuration of P, As and Sb**

*The only pentahalide of bismuth known is  $BiF_5$*

The pentahalides of bismuth are however less stable due to inert pair effect. However bismuth pentafluoride is reasonably stable. Chlorides of group VA elements are generally familiar. All trihalides of group VA are known, but only seven pentahalides are reported.  $BiF_3$  is ionic and all other halides are covalent. These halides are listed in Table 1.8.

**Table 1.8 Halides of the group VA elements**

Element	Trihalides	Pentahalides
Nitrogen	$NF_3$ , $NCI_3$ , $NBr_3$ , $NI_3$	—
Phosphorus	$PF_3$ , $PCl_3$ , $PBr_3$ , $PI_3$	$PF_5$ , $PCl_5$ , $PBr_5$
Arsenic	$AsF_3$ , $AsCl_3$ , $AsBr_3$ , $AsI_3$	$AsF_5$ , $(AsCl_5)$
Antimony	$SbF_3$ , $SbCl_3$ , $SbBr_3$ , $SbI_3$	$SbF_5$ , $SbCl_5$
Bismuth	$BiF_3$ , $BiCl_3$ , $BiBr_3$ , $BiI_3$	$BiF_5$

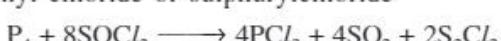
Nitrogen halides are normally obtained by the action of excess of halogen on ammonia.

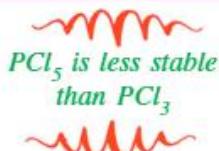


Phosphorus trichloride is obtained by passing dry chlorine over heated white phosphorus. Phosphorus pentachloride is obtained with excess chlorine. Phosphorus trifluoride is formed when fluorine reacts with phosphorus trichloride.

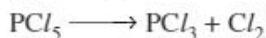


Chlorides of phosphorus are also obtained from phosphorus by the action of thionyl chloride or sulphurylchloride



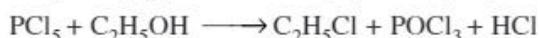
  
*PCl<sub>5</sub> is less stable than PCl<sub>3</sub>*

PCl<sub>3</sub> is more stable than PCl<sub>5</sub>. On warming, PCl<sub>5</sub> sublimes, but decomposes on strong heating and liberates chlorine.



PCl<sub>5</sub> exists as ionic solid, [PCl<sub>4</sub>]<sup>+</sup> [PCl<sub>6</sub>]<sup>-</sup>. [PCl<sub>4</sub>]<sup>+</sup> is tetrahedral and [PCl<sub>6</sub>]<sup>-</sup> is octahedral. In liquid or vapour states, PCl<sub>5</sub> has trigonal bipyramidal structure.

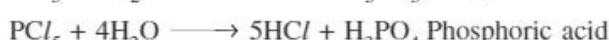
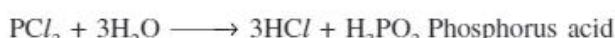
Both PCl<sub>3</sub> and PCl<sub>5</sub> are used in the synthesis of ethyl chloride and acetyl chloride.



All the halides of the group VA are covalent, except BiF<sub>3</sub>. These halides undergo hydrolysis, except NF<sub>3</sub>. Hydrolysis of NCl<sub>3</sub> gives ammonia and hypochlorous acid. Aqueous NCl<sub>3</sub> acts as a bleaching agent.



Trihalides of phosphorus and arsenic undergo hydrolysis to give the corresponding -ous acids. Pentahalides of phosphorus and arsenic undergo hydrolysis to give corresponding -ic acids.



Trihalides of bismuth and antimony undergo partial hydrolysis to give the corresponding oxyhalides (eg : BiOCl). The extent of hydrolysis decreases from halides of nitrogen to bismuth. This decrease also supports the increase in the metallic nature of the elements going down the group.

Finely divided metals on heating with PCl<sub>5</sub> give corresponding chlorides.



Trihalides use the sp<sup>3</sup> hybridised orbitals of the central atom. They have ammonia like trigonal monopyramidal structure. Pentahalides use the sp<sup>3</sup>d hybridised orbitals of the central atom. They have trigonal bipyramidal structure as shown in Fig 1.6.

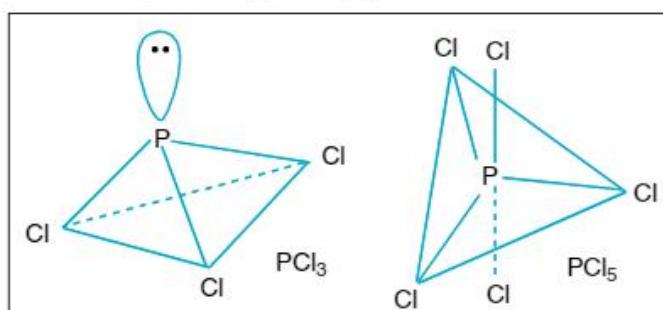


Fig 1.6 Structures of chlorides of phosphorus



**P.1.9** Both  $\text{PH}_3$  and  $\text{NH}_3$  are Lewis bases, but basic strength of  $\text{PH}_3$  is less than that of  $\text{NH}_3$ . Explain.

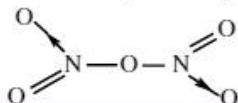
**Solution** 'N' atom of  $\text{NH}_3$  or 'P' atom of  $\text{PH}_3$  has a lone pair of electrons available for donation. Hence  $\text{NH}_3$  and  $\text{PH}_3$  are Lewis bases. The electron pair density on a larger 'P' atom is less than that on smaller 'N' atom. Hence  $\text{PH}_3$  is a weaker base.



**P.1.10** What is the covalency of 'N' in nitrogen pentoxide?

**Solution** Number of 'O' atoms bonded to each 'N' atom in  $\text{N}_2\text{O}_5$  is 2.5. Hence the covalency of 'N' is calculated as 5, based on oxide theory.

But by the examination of the structure of  $\text{N}_2\text{O}_5$ , one can observe that 'N' forms only 4 bonds. Its covalency in nitrogen pentoxide is 4.



**P.1.11** Both NO and  $\text{NO}_2$  have odd number of electrons. NO is colourless, but  $\text{NO}_2$  is coloured. Why?

**Solution** In  $\text{NO}_2$  molecule, colour is explained based on the presence of unpaired electron, which can be excited easily by the absorption of visible light. In NO molecule, the odd electron is also involved in bonding between two bonded atoms, the excitation of which can be possible only in ultraviolet region. Thus NO is colourless.



**P.1.12** The magnetic properties of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are different. Why?

**Solution**  $\text{NO}_2$  molecule has unpaired electron. Hence it is paramagnetic and reactive.  $\text{NO}_2$  dimerises to give  $\text{N}_2\text{O}_4$ .  $\text{N}_2\text{O}_4$  molecule has no unpaired electrons. Hence it is diamagnetic.



**P.1.13**  $\text{PCl}_5$  is less stable. Why?

**Solution**  $\text{PCl}_5$  molecule has trigonal bipyramidal structure. The three equatorial bonds are equivalent. The P-Cl bond length in equatorial position is 202 pm. The two axial bonds (240 pm) are longer.

The axial bonds suffer more repulsion as compared to the equatorial bonds.

Hence,  $\text{PCl}_5$  is less stable.



**P.1.14**  $\text{PCl}_3$  is covalent. It fumes in moisture and its aqueous solution is electrical conductor. Why?

**Solution**  $\text{PCl}_3$  hydrolyses in moisture (or in water) giving fumes of hydrogen chloride.



In aqueous solutions, HCl ionises and hence acts as electrical conductor.



**P.1.15** What happens when phosphine is absorbed in mercuric chloride solution?

**Solution** Mercuric phosphide is formed by the reaction between phosphine and mercuric salt.



**P.1.16** Phosphine is technically used in Holme's signals. Substantiate.

**Solution** Spontaneous combustion of phosphine is used in Holme's signals. Tins containing calcium carbide and calcium phosphide are thrown in sea. Acetylene and phosphine gases are evolved, which will burn and serve as a signal.



**P.1.17** In the preparation of  $\text{P}_4\text{O}_6$ , a mixture of  $\text{N}_2$  and  $\text{O}_2$  is used rather than pure  $\text{O}_2$ , Why?

**Solution** Pure oxygen will oxidise  $\text{P}_4\text{O}_6$  to  $\text{P}_4\text{O}_{10}$  despite an excess of  $\text{P}_4$  is kept at the start of the reaction. Hence, nitrogen gas is used as a diluent.



**P.1.18** Pentahalides of phosphorous are known, but not pentahydride. Why?

**Solution** Phosphorous exhibits pentavalency in excited state. Fluorine, chlorine or bromine is more electronegative and influences excitation to form  $\text{PX}_5$ . However, hydrogen is not that much electronegative to influence the excitation in phosphorus. Hence  $\text{PH}_5$  is not formed.



**P.1.19** The bond angle in  $\text{PH}_4^+$  is higher than that in  $\text{PH}_3$ . Why?

**Solution** In  $\text{PH}_4^+$ , phosphorous undergo  $\text{SP}^3$  hybridization, but in  $\text{PH}_3$  phosphorous uses pure p-orbitals for bonding. Hence bond angle in  $\text{PH}_3$  is nearly  $90^\circ$ .



### EXERCISE - 1.1.2

1. Discuss the basic strength and stability of hydrides of group 15.
2. Write different oxides of nitrogen. Mention the oxidation states of nitrogen in these oxides.
3. Write the structures of the oxides :  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$ .
4. Write the hydrolysis reactions of the halides :  $\text{NCI}_3$ ,  $\text{PCl}_3$  and  $\text{PCl}_5$ .

## OXY ACIDS

Oxyacid is a ternary compound of hydrogen, oxygen and non-metallic element. Elements of group VA form two important types of oxyacids. The oxyacid with lower oxidation state is usually called –ous acid and the one with higher oxidation state is called –ic acid.

### 1.3.1

#### Oxyacids of nitrogen

Nitrogen forms four important oxyacids, which are listed in Table 1.9.

Table 1.9 Oxyacids of nitrogen

Oxyacid	Chemical formula	Oxidation state of N	Basicity
Hyponitrous acid	$\text{H}_2\text{N}_2\text{O}_2$	+1	2
Nitrous acid	$\text{HNO}_2$	+3	1
Nitric acid	$\text{HNO}_3$	+5	1
Pernitric acid	$\text{HNO}_4$	+5	1

Hyponitrous acid is regarded as a dimer of  $\text{HNO}$ . It has the  $-\text{N}=\text{N}-$  group. It is less stable. It is the only dibasic acid of nitrogen.

Nitrous acid is less stable. It exists only in solutions. It undergoes disproportionation to give  $\text{HNO}_3$  and  $\text{NO}$ . The anhydride of nitrous acid is nitrogen trioxide.

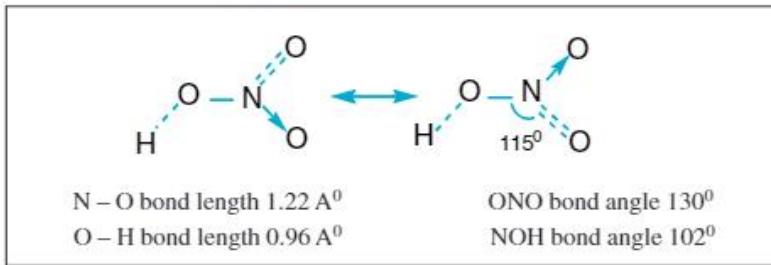
Nitrous acid is a weak acid. It acts as oxidant as well as reductant. It acts as oxidant to  $\text{SnCl}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , etc., but as reductant to stronger oxidants like  $\text{KMnO}_4$ ,  $\text{F}_2$ ,  $\text{Br}_2$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , etc. Salts of nitrous acid are called nitrites. Nitrite has angular structure. Nitrous acid is used to identify aromatic amines from aliphatic amines.

Nitrous acid exists in two tautomeric forms. They are nitro ( $\text{H}-\text{NO}_2$ ) and nitrite ( $\text{HO}-\text{N}=\text{O}$ ), in which nitrite form is acidic.

*$\text{HNO}_2$  acts as oxidant as well as reductant*

*Anhydride of  
HNO<sub>3</sub> is N<sub>2</sub>O<sub>5</sub>*

Nitric acid is more stable than nitrous acid. Anhydride of nitric acid is nitrogen pentoxide. It is a strong acid and is called mineral acid. Its salts are called nitrates. Gaseous nitric acid is a planar molecule. Nitric acid is supposed to exist in two resonating forms as shown in Fig 1.7.



**Fig 1.7 Structures of nitric acid**

Pernitric acid is unstable. It has a O–O linkage. It is a monobasic acid. It also acts as an oxidant.

### 1.3.2

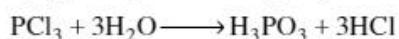
#### Oxyacids of phosphorus

*H<sub>3</sub>PO<sub>3</sub> is a weak  
dibasic acid*

Phosphorus forms a number of oxyacids. Four –ous acids and five –ic acids are known. Some common oxyacids of phosphorus are listed in Table 1.10 and Table 1.11.

Hypophosphorous acid and meta-phosphoric acids are monobasic, while hypophosphoric acid and pyrophosphoric acid are tetrabasic acids. Since hypophosphorus acid is monobasic, it cannot form acidic salt.

Phosphorus acid is prepared by dissolving phosphorus trioxide or phosphorus trichloride in water. The structure of phosphorus acid is shown in Fig 1.8. Phosphorus acid is a weak and dibasic acid. It forms two series of salts such as NaH<sub>2</sub>PO<sub>3</sub> and Na<sub>2</sub>HPO<sub>3</sub> respectively. NaH<sub>2</sub>PO<sub>3</sub> is known as primary phosphite and Na<sub>2</sub>HPO<sub>3</sub> as secondary phosphites.



**Table 1.10 Oxyacids of phosphorus (–ous acids)**

Name of the acid	Formula of acid	Oxidation state of 'P'	Characteristic bonds	Preparation of acid
Hypophosphorous acid	H <sub>3</sub> PO <sub>2</sub>	+1	One P–OH Two P–H One P=O	white P <sub>4</sub> + alkali + acid
Orthophosphorous acid	H <sub>3</sub> PO <sub>3</sub>	+3	Two P–OH One P–H One P=O	P <sub>2</sub> O <sub>3</sub> + H <sub>2</sub> O
Pyrophosphorous acid	H <sub>4</sub> P <sub>2</sub> O <sub>5</sub>	+3	Two P–OH Two P–H Two P=O	PCl <sub>3</sub> + H <sub>3</sub> PO <sub>3</sub>

Table 1.11 Oxyacids of phosphorus (-ic acids)

Name of the acid	Formula of acid	Oxidation state of 'P'	Characteristic bonds	Preparation of acid
Hypophosphoric acid	$\text{H}_4\text{P}_2\text{O}_6$	+4	Four P-OH Two P=O One P-P	red $\text{P}_4$ + alkali + acid
Orthophosphoric acid	$\text{H}_3\text{PO}_4$	+5	Three P-OH One P=O	$\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$
Pyrophosphoric acid	$\text{H}_4\text{P}_2\text{O}_7$	+5	Four P-OH Two P=O One P-O-P	heat phosphoric acid
Metaphosphoric acid	$(\text{HPO}_3)_3$ Trimer	+5	Three P-OH Three P=O Three P-O-P	Phosphorus acid + $\text{Br}_2$ , heat in a sealed tube
Peroxyphosphoric acid	$\text{H}_3\text{PO}_5$	+5	Three P-OH One P=O One O-O	Phosphoric acid + $\text{H}_2\text{O}_2$

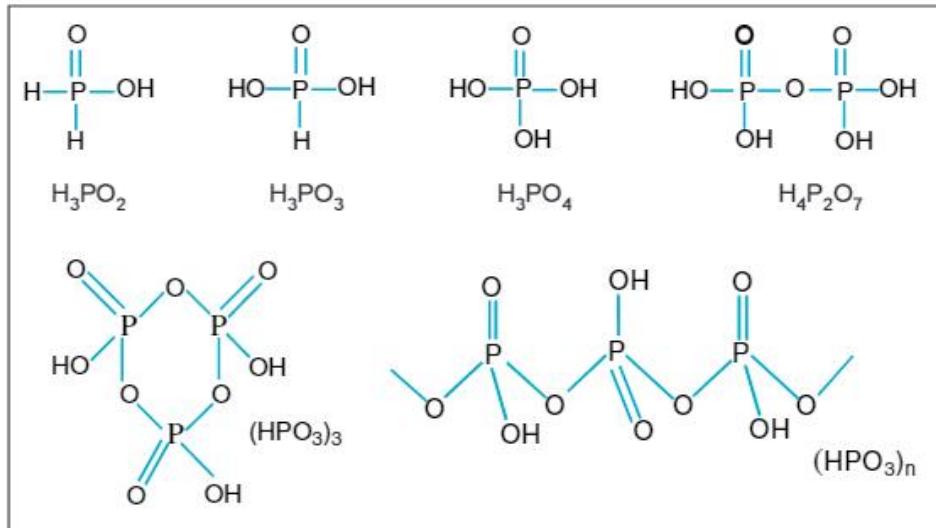
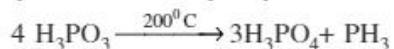


Fig 1.8 Structures of oxyacids of phosphorus

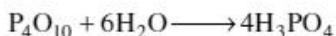
Orthophosphorus acid acts as a strong reducing agent. It reduces  $\text{CuSO}_4$  to Cu,  $\text{AgNO}_3$  to Ag,  $\text{HgCl}_2$  to  $\text{Hg}_2\text{Cl}_2$ ,  $\text{I}_2$  to HI and acidified  $\text{KMnO}_4$  solution.

Orthophosphorus acid on heating undergoes disproportionation to give phosphine and orthophosphoric acid.



Orthophosphoric acid is commonly called phosphoric acid. It is prepared by dissolving phosphorus pentoxide or phosphorus pentachloride in water. It is prepared on a large scale from bone ash or from phosphorite by treating with sulphuric acid.

*On a large scale  
phosphoric acid is  
prepared from  
phosphorite*

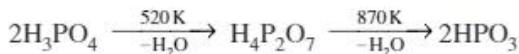


By heating red phosphorus with concentrated nitric acid, phosphoric acid is best prepared in the laboratory.

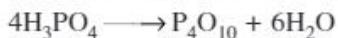


Phosphoric acid is a weak and tribasic acid. It forms three series of salts such as  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_3\text{PO}_4$  known as primary phosphate, secondary phosphate and tertiary phosphate.  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  are acidic salts, but  $\text{Na}_3\text{PO}_4$  is a normal salt. Calcium super phosphate is a primary phosphate and is a common phosphatic fertiliser.

Orthophosphoric acid on heating loses water in steps forming pyro-phosphoric and metaphosphoric acids.



When strongly heated at red hot,  $\text{P}_4\text{O}_{10}$  is formed.



Orthophosphates are identified in the molybdate test as canary yellow ammonium phosphomolybdate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12(\text{MoO}_3)$

Pyrophosphoric acid is formed by heating an equimolar mixture of ortho and meta phosphoric acids at  $100^\circ\text{C}$ . Hypophosphorus acid,  $\text{H}_4\text{P}_2\text{O}_6$  has P-P linkage. Perphosphoric acid,  $\text{H}_3\text{PO}_5$  has O-O peroxy linkage.

Metaphosphoric acid is a glassy transparent solid called glacial phosphoric acid. Sodium hexametaphosphate is called calgon and is used as water softner.

The number of  $-\text{OH}$  groups determines the basicity of the acid and the number of P-H bonds denotes the reduction ability of the oxyacid. Thus hypophosphorus acid is a stronger reductant and gives metallic silver with silver nitrate.



Aqueous hypophosphorus acid reduces benzene diazonium salt to benzene. Phosphorus acid also reduces aqueous metallic salts to precipitate metals (like Cu, Hg).

In general phosphorus undergoes  $\text{sp}^3$  hybridisation and has tetrahedral geometry in its oxyacid. Phosphorus usually forms five bonds.

### 1.3.3

#### Anamolous behaviour of nitrogen

The following are the important points in which nitrogen differs from the rest of the group VA elements.

1. Nitrogen is a gas, while other elements of the group VA are solids at room temperature.
2. Nitrogen is a diatomic molecule, while phosphorus, arsenic and antimony are tetra-atomic molecules. Nitrogen molecule alone has the ability to form  $\pi$ -bonds, while in other molecules the bond order is one.



**Nitrogen forms many oxides**



**Nitrogen has -3 state in nitride**



**Nitrogen is chemically inert, due to high bond energy**



3. The hydride of nitrogen,  $\text{NH}_3$  is stable and has intermolecular hydrogen bonding. Hydrides of other elements are reactive.
4. Nitrogen does not form pentahalide, while P, As and Sb form pentahalides.
5. Nitrogen forms many oxides, but for other elements only tri and pentoxides are important.
6. Nitrogen predominantly exhibits -3 oxidation state, while for other elements +3 and +5 states are important.
7. Nitrogen is regarded as inert gas, due to high triple bond energy, while other elements are reactive.
8. Nitrogen cannot form  $d_{\pi} - p_{\pi}$  bond as the heavier elements can. e.g.  $\text{R}_3\text{P}=\text{O}$  or  $\text{R}_3\text{P}=\text{CH}_2$  (where R is alkyl group). Phosphorus and arsenic can form  $d_{\pi} - p_{\pi}$  bond even with transition elements when their compounds like  $\text{P}(\text{C}_2\text{H}_5)_3$ ,  $\text{As}(\text{C}_6\text{H}_5)_3$  etc. act as liquids.

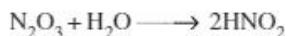
The abnormal behaviour of nitrogen and the difference in the properties listed above are mainly due to the following factors.

1. Small size of nitrogen atom and absence of valence d-orbitals in nitrogen atom.
2. High value of electronegativity of nitrogen.
3. Tendency of forming multiple bonds by nitrogen atom.
4. Having only two electrons in the perultimate shell of nitrogen.



**P.1.20** Mention which oxyacids  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{O}_5$  are anhydrides?

**Solution**  $\text{N}_2\text{O}_3$  is anhydride of nitrous acid and  $\text{N}_2\text{O}_5$  is anhydride of nitric acid.  $\text{N}_2\text{O}_4$  is a mixed anhydride of nitrous acid and nitric acid.



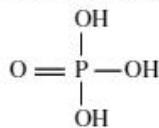
**P.1.21**  $\text{HNO}_3$  is an oxidising agent but  $\text{H}_3\text{PO}_4$  is not. Explain.

**Solution** The inability of nitrogen atom to unpair and promote its 2s-electron results in the pentapositive state of nitrogen being less stable than tripositive. Thus,  $\text{HNO}_3$  where nitrogen is in +5 oxidation state is an oxidizing agent. On the other hand P has d-orbitals to expand its octet and also shows no inert pair effect, is quite stable in V state. Thus,  $\text{H}_3\text{PO}_4$  in which P is in +5 oxidation state is not oxidizing.



**P.1.22** What is the basicity of orthophosphoric acid ? Write the types of salts formed by it.

**Solution** Orthophosphoric acid,  $\text{H}_3\text{PO}_4$  has three -OH groups and its basicity is 3



Orthophosphoric acid,  $\text{H}_3\text{PO}_4$  forms three types of salts.

$\text{H}_2\text{PO}_4^-$  is the anion of primary salt, an acidic salt.  $\text{HPO}_4^{2-}$  is the anion of secondary salt, an acidic salt.  $\text{PO}_4^{3-}$  is the anion of tertiary salt, normal salt.



**P.1.23** Based on the structures how is the reduction ability of  $\text{H}_3\text{PO}_2$  or  $\text{H}_3\text{PO}_3$  accounted for?

**Solution**  $\text{H}_3\text{PO}_2$  has two P-H bonds. The two H atoms linked directly to central P atom imparts reducing character to the acid. Similarly  $\text{H}_3\text{PO}_3$  has one P-H bond, imparting reduction ability.



**P.1.24** How is tautomerism different from resonance?

**Solution** The skeleton of atoms in any molecule does not change in resonance. Only the pi electrons undergo delocalisation.

Tautomerism involves the migration of atoms and the isomers are in dynamic equilibrium.

### EXERCISE - 1.1.3

1. Write on the structural aspects of nitrous and nitric acids.
2. Mention the oxyacids of phosphorus and the oxidation states of phosphorus.
3. Comment on the acidic nature of phosphoric acid
4. Nitrogen behaves different from rest of the elements of the same group. Explain.

## AMMONIA, NITROUS ACID AND NITRIC ACID

### 1.4.1

#### Ammonia Structure :

The central atom in ammonia undergoes  $\text{sp}^3$  hybridisation. Ammonia has 3 bond pairs and one lone pair of electrons. It has trigonal pyramidal structure with nitrogen atom at the apex as shown in Fig 1.9.

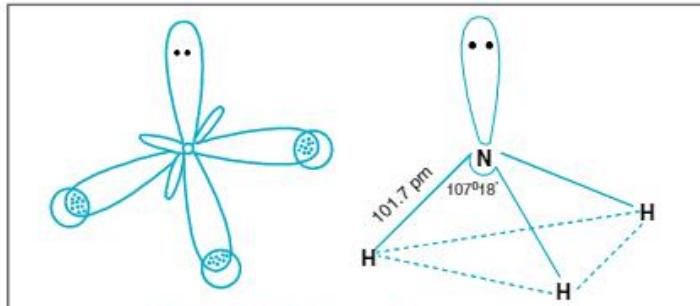
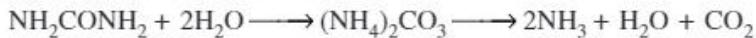


Fig 1.9 Structure of ammonia

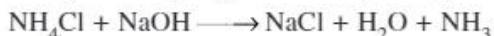
Due to the tetrahedral hybridisation, the bond angle in  $\text{NH}_3$  is expected to be  $109^\circ 28'$ . The observed bond angle in  $\text{NH}_3$  is  $107^\circ 18'$ . The decrease in the bond angle is attributed to the presence of a lone-pair on nitrogen atom and greater repulsions between lone-pair and bond pairs.

#### Preparation

In small quantities ammonia is present in air and soil as a result of decay of nitrogenous organic matter e.g., urea.



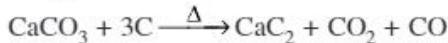
Ammonia can be prepared in the laboratory by the action of dry slaked lime or caustic soda on an ammonium salt.



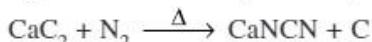
On large scale ammonia can be prepared by (i) Cyanamide method or (ii) Haber's synthesis or (iii) Destructive distillation of coal.

In the cyanamide process, lime stone or lime is heated strongly with excess coke to get calcium carbide.

*Nitrolim is a mixture of calcium cyanamide and graphite*



Calcium carbide on heating at 1000–1100°C in a stream of nitrogen gives a mixture of calcium cyanamide and graphite, called nitrolim. Nitrolim can be used directly as a fertiliser. Cyanamide ( $\text{-N}=\text{C}=\text{N}-$ ) is isostructural with carbon dioxide.

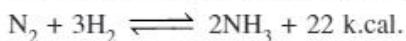


Calcium cyanamide on treating with superheated steam at 180°C gives ammonia.



In the Haber's synthesis, ammonia is prepared from its elements hydrogen and nitrogen in the volume ratio, 3:1. The flow chart block diagram of Haber's method is shown in Fig 1.10.

The reaction between nitrogen and hydrogen to give ammonia is reversible.



The favourable conditions for the Haber's synthesis are :

- High pressure, 200–400 atm.
- Moderate (optimum working) temperature of 450 – 500°C.
- Use of iron as catalyst and molybdenum (or K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>) as promoter.

The raw materials, nitrogen and hydrogen, are mixed in 1:3 volume ratio. The mixture is compressed to over 200 atmospheres pressure and then introduced into the reaction bed containing the catalyst. The mixture is allowed to react at 450–500°C. The reaction mixture, with about 10% ammonia, is cooled to get the liquid ammonia. The liquid is tapped out. The unreacted gases are recirculated to the reaction bed.

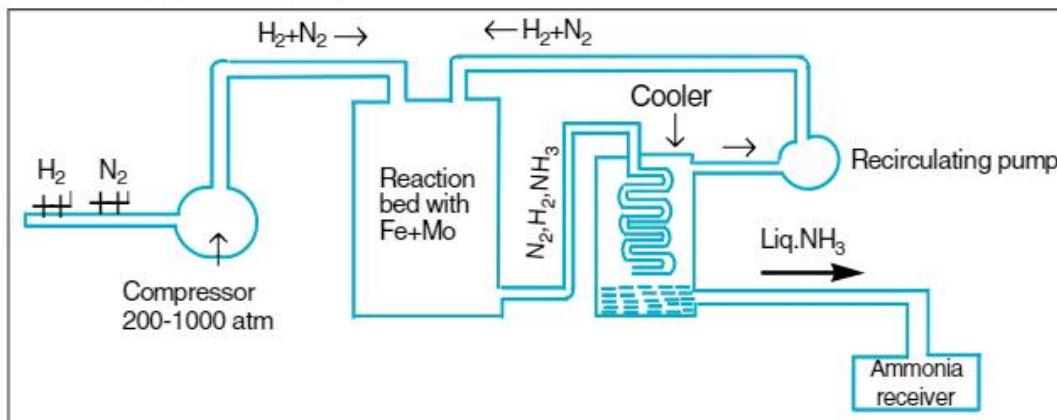


Fig 1.10 Flow chart block diagram of ammonia synthesis

#### Properties

Ammonia is a colourless gas with pungent characteristic smell. It freezes at 198 K and boils at 240 K. It is highly soluble in water.

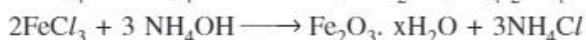


  
**Ammonia is dried over quick lime**  

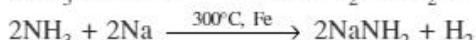
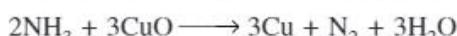

Ammonia is a Lewis base. Due to its basic nature, it cannot be dried over sulphuric acid, phosphorus pentoxide or anhydrous calcium chloride. Quick lime is used to dry ammonia. Ammonia forms salts with acids.



Ammonia precipitates metal hydroxides from their salt solutions.



Ammonia acts as a reductant, when it reacts with cupric oxide and as acid when heated with an active metal like sodium.



Ammonia has a lone pair of electrons on the central atom and acts as Lewis base. It is a ligand and forms complex compounds with metal ions, a blue complex with  $\text{Cu}^{2+}$  and colourless complex with  $\text{Ag}^+$ .



#### Uses

1. Liquid ammonia is a good solvent for ionic substances as well as for covalent substances.
2. Ammonia is used in the manufacture of fertilisers like urea, ammonium sulphate, calcium ammonium nitrate, etc.
3. Ammonia is used as a refrigerant and as a reagent for the detection of ions like  $\text{Cu}^{2+}$  cation,  $\text{Ag}^+$  cation, etc.

#### 1.4.2

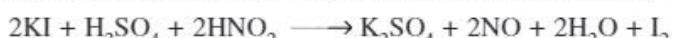
#### Nitrous acid

Free nitrous acid is unknown and is known only in solution. A solution of nitrous acid can be prepared by acidifying solutions of nitrites with mineral acids.



Nitrous acid is a weak monobasic acid. It decomposes into nitric oxide and nitrogen dioxide and heating. Nitrous acid acts as an oxidising agent and reducing agent.

**Oxidising nature :** Nitrous liberates iodine from potassium iodide.

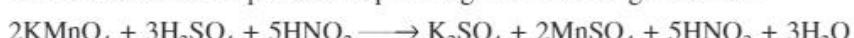


Nitrous acid oxidises sulphur dioxide to sulphuric acid and sulphide to sulphur. It oxidises stannous chloride to stannic chloride, acidified ferrous sulphate to ferric sulphate, sodium arsenite to arsenate etc.,

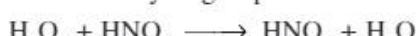
**Reducing nature :** Nitrous acid reduces bromine to hydrobromic acid



It reduces acidified potassium permanganate to manganous ion



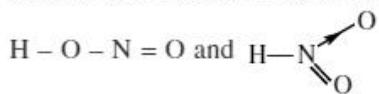
It reduces hydrogen peroxide to water



  
**Nitrous acid acts as oxidant as well as reductant**  


**Structure :**

Nitrous acid is considered to be a factomeric mixture of two forms:

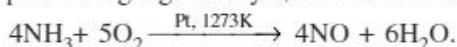
**1.4.3****Nitric acid**

Nitric acid is the most important oxyacid of nitrogen. It is prepared in the laboratory by heating potassium or sodium nitrate with concentrated sulphuric acid.

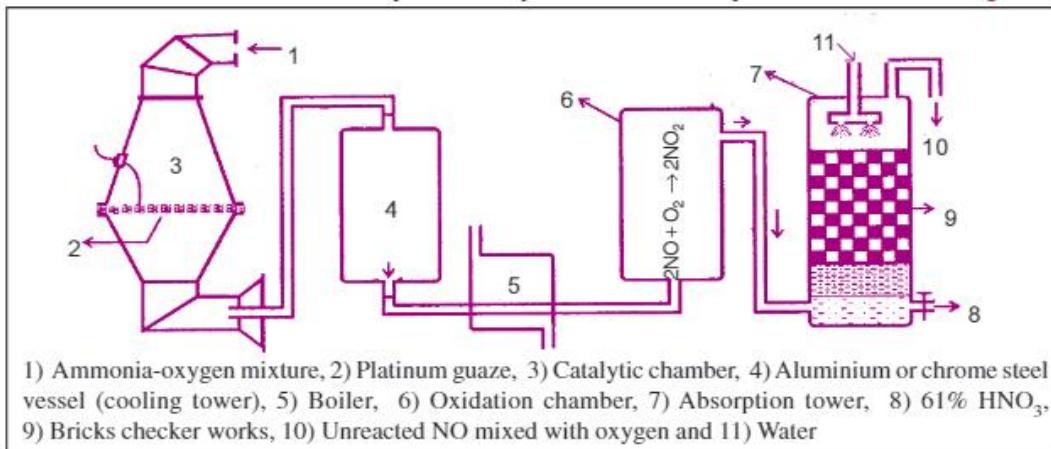


Nitric acid is manufactured on a large scale by Ostwald's process or Birkland and Eyde's process.

In Ostwald's process ammonia is mixed with air in 1:7 ratio, when passed over hot platinum gauge catalyst, ammonia is oxidised to nitric oxide.

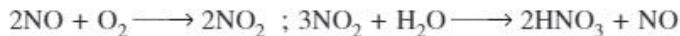


The liberated heat keeps the catalyst hot. Ostwald's process is shown in Fig 1.11.



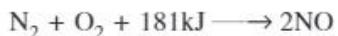
**Fig 1.11 Flow chart diagram of Ostwald's process**

Nitric oxide thus formed combines with oxygen to give nitrogen dioxide, which is dissolved in water under pressure to give nitric acid.



Nitric oxide thus formed is recycled. Dilute nitric acid obtained in Ostwald's method can be concentrated by distillation up to 68%. The concentration of nitric acid is improved to 98% by dehydration with concentrated sulphuric acid. Pure nitric acid crystals are obtained by cooling in a freezing mixture.

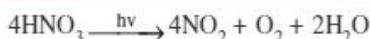
In Birkland and Eyde's process, air is converted to nitric oxide at an electric arc.



Nitric oxide is oxidised to nitrogen dioxide. In an absorption tower, filled with quartz pieces, dioxide is made to react with further air and water to form nitric acid.

HNO<sub>3</sub> is colourless but often gradually turns yellow. Yellow colour is produced due to the fact that HNO<sub>3</sub>, when exposed to light, undergoes decomposition to form nitrogen dioxide which dissolves in HNO<sub>3</sub> and gives yellow colour. The yellow colour can be removed by warming it upto 60-80°C and buffling dry air.

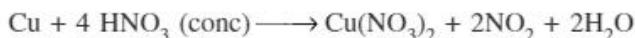
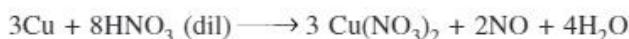
*In Birkland and Eyde's process, NO is obtained from air at an arc*



Nitric acid is a strong acid and acts as a strong oxidant. Iodine is oxidised to iodic acid, sulphur to sulphuric acid and phosphorus to phosphoric acid.



It attacks metals, except noble metals such as Au and Pt. The products of the oxidation reaction depend upon concentration of acid, temperature and electropositivity of metal.



  
**Nitration mixture is**  
**a 1:1 mixture of**  
**conc  $\text{HNO}_3$**   
**and conc  $\text{H}_2\text{SO}_4$**   


Some metals like Al, Cr, etc., are passive to concentrated nitric acid due to the formation of protective oxide film.

The main use of nitric acid is to manufacture ammonium nitrate fertilisers. Other nitrates are used for pyrotechnics and explosives like ammonal, nitroglycerin and trinitrotoluene.

In laboratory a 1:1 mixture of concentrated nitric acid and concentrated sulphuric acid is used as nitration mixture. It is used in the preparation of artificial silk (cellulose nitrate), perfumes, dyes and medicines.

Other major uses of nitric acid are in the pickling of metal surfaces, etching of metals and an oxidiser in rocket fuel. Nitric acid is used as oxidant in preparing terephthalic acid from paraxylene and adipic acid (hexanedioic acid) from cyclohexene or cyclohexanol or cyclohexanone.



**P.1.25** Ammonia cannot be dried over anhydrous calcium chloride. Why?

**Solution** When water is absorbed by calcium chloride, it undergoes hydrolysis to give hydrochloric acid.  
 $\text{CaCl}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + 2\text{HCl}$

Since ammonia is basic, it is neutralised by HCl to give salt. Hence ammonia is dried over a basic oxide, quick lime.



**P.1.26** Coal is a potential source for ammonia. Comment.

**Solution** Coal on destructive distillation gives coal tar, which also contains ammonical liquor.

When the liquid is treated with milk of lime and steam is blown, ammonia gas is evolved. Concentrated ammonia solution can be prepared by dissolving in steam directly. A fertiliser ammonium sulphate is obtained when ammonia is absorbed in  $\text{H}_2\text{SO}_4$ .



**P.1.27** Nitric acid acts as oxidant, while nitrous acid as both oxidant and reductant. Why?

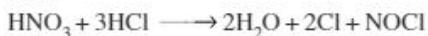
**Solution** In  $\text{HNO}_3$ , the oxidation state of 'N' is +5, highest for 'N'. N can be converted only into lower states. Hence  $\text{HNO}_3$  acts as oxidising agent.

In  $\text{HNO}_2$ , the oxidation state of 'N' is +3. It can be lowered or raised. Hence  $\text{HNO}_2$  can act as oxidising as well as reducing agent.



**P.1.28** What is aqua-regia? How it works to dissolve noble metals?

**Solution** Aqua-regia is 3:1 mixture of conc.  $\text{HNO}_3$  and conc.  $\text{HCl}$ . The mixture contains nascent chlorine produced due to reduction of  $\text{HCl}$  by  $\text{HNO}_3$ . This chlorine reacts with noble metals to dissolve them.



**P.1.29**  $\text{Al}_2\text{O}_3 + \text{N}_2 + \text{C} \longrightarrow \text{X} + \text{CO} ; \text{X} + \text{H}_2\text{O} \longrightarrow \text{Y} + \text{Z}$

'Y' is an amphoteric substance. When aqueous 'Z' is treated with  $\text{AlCl}_3$  solution again 'Y' is formed. What are X, Y and Z?

**Solution**  $\text{X} = \text{Al/N}$ , which on hydrolysis gives  $\text{Al(OH)}_3$  and ammonia.  $\text{Y} = \text{Al(OH)}_3$  and  $\text{Z} = \text{NH}_3$

Ammonium chloride precipitates aluminium hydroxide with aqueous ammonia.



### EXERCISE - 1.1.4

1. Describe the manufacture of ammonia by Haber's method. Give a labelled block diagram.
2. How is ammonia prepared in cyanamide process?
3. Discuss the principle of preparing nitric acid in Ostwald's process. Give the necessary equations.
4. Nitrous acid acts as oxidant as well as reductant. Give suitable examples.
5. How is nitric acid prepared on a large scale by Birkland and Eyde's process? Write the principle and equations.
6. Write the important uses of (a) ammonia and (b) nitric acid.



1. Nitrogen, phosphorus, arsenic, antimony and bismuth are the elements of group 15 and are called elements of nitrogen family.
2. The general electronic configuration of group 15 elements is  $\text{ns}^2\text{np}^3$ , with half filled p-sub-shells.
3. Nitrogen is a gas at room temperature, while other elements of the group VA are solids.
4. Nitrogen is the most abundant element in the earth's atmosphere, 78% by volume and 75% by weight.
5. Common mineral of nitrogen is salt petre and that of phosphorus is phosphorite.
6. Nitrogen is diatomic, while phosphorus, arsenic and antimony are tetraatomic.
7. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a metal.

8. Except bismuth, all elements of group 15 exhibit allotropy.
9. Nitrogen is chemically inert, due to high dissociation energy of triple bond.
10. The maximum covalency of nitrogen is 4. Nitrogen cannot exhibit pentavalency, due to lack of valence d- orbitals.
11. The element that exhibits maximum types of oxidation numbers is nitrogen. The values range between -3 and +5.
12. Ammonia has trigonal pyramidal shape. The central atom of ammonia undergoes  $sp^3$  hybridisation. The bond angle is 107, due to the presence of a lone pair on the central atom.
13. Ammonia is relatively more stable and less reactive, due to relatively stronger N-H bond.
14. Nitrogen forms many oxides.  $N_2O$  and NO are neutral oxides. Most acidic oxide of nitrogen is nitrogen pentoxide.
15. NO and  $NO_2$  are paramagnetic due to the presence of unpaired electrons.
16. The most stable halide of nitrogen is nitrogen trifluoride.
17. Orthophosphoric acid is tribasic. It forms two acidic salts and one normal salt.
18. The abnormal properties of nitrogen are due to small size, high electronegativity and absence of valence d-orbitals.
19. Ammonia is synthesised by Haber's method at high pressure, moderate temperature and in the presence of iron catalyst.
20. Nitric acid is commercially prepared by the oxidation of ammonia in Ostwald's process.
21. Metals like Al, Cr, etc. are passive to concentrated nitric acid, due to the formation of protective oxide film.

### **EXERCISE - 1.2**

1. Discuss the structure and bonding in  $P_4$  molecule.
2. What is allotropy? Write the allotropes of phosphorus.
3. Comment on the M-M bond strengths and catenation ability of group 15 elements.
4. Elemental phosphorus is not diatomic like nitrogen. Explain.
5. Write differences between white phosphorus, red phosphorus and black phosphorus?
6. Mention the oxidation numbers of nitrogen with suitable examples.
7. Nitrogen is trivalent, but phosphorus is pentavalent in its compounds. Explain.
8.  $PH_3$  is stable in air, but catches fire when heated at 425K. Why?
9. Discuss the stability of hydrides of group 15 elements.
10. Write the trends in bond length, bond angle, and boiling points of  $MH_3$  type hydrides.
11. Nitrogen forms several oxides. Why?
12. Nitrous oxide supports combustion more vigorously than air. Why?

## CHEMISTRY IIC

13. In case of phosphorus trihalides, bond angle increases from  $\text{PF}_3$  to  $\text{PI}_3$ . Why?
14.  $\text{NH}_3$  and  $\text{NF}_3$  are both pyramidal. What observations are made on the difference in bond angles, bond polarities and dipolemoments?
15. The correct order of bond angles is  $\text{NO}_2^+ > \text{NO}_2 > \text{NO}_2^-$ . Discuss.
16. Copper metal gives different products on reaction with nitric acid. Illustrate.
17. Discuss the structure and basicity of orthophosphorus acid.
18. Draw the structures of -ous acids of phosphorus and discuss their reduction ability.
19. What happens when the following are heated?
  - (a) orthophosphoric acid and (b) sodiumdihydrogen orthophosphate.
20. Nitrogen behaves abnormally from the other elements of the same group. Discuss?
21. Trimethylamine is a stronger base than trisilylamine. Justify.
22. What is the ratio of product gases, nitric oxide and nitrogen dioxide formed when phosphorus is treated to nitrite acid? (Ans : 1 : 1)
23. Concentrated nitric acid turns yellow in sunlight. Why? (Hint : Formation of  $\text{NO}_2$ )
24. How the products of oxidation of metals with nitric acid depend?
25. How is ammonia prepared from lime and coke?
26. Discuss the conditions for Haber's ammonia synthesis.
27. Ammonia is used as refrigerant. Why?
28. Though N–F in  $\text{NF}_3$  is a polar bond, the experimental bond length is greater than the theoretically predicted value. Explain.
29. A waxy crystalline solid (X) with a garlic odour is obtained by burning white phosphorus in air. X reacts vigorously with hot water forming an acid and gas Y. Y is neutral towards litmus and produces a black residue Z when passed through cupric sulphate. What are Y and Z? (Ans :  $\text{PH}_3$ ,  $\text{Cu}_3\text{P}_2$ )
30. Compound 'A' is an unstable pale blue solution of an acidic oxide. 'A' decolourises bromine water as well as acidified permanganate. 'A' oxidises stannous chloride in hydrochloric acid solutions. Predict the acid 'A' and its unhydride. (Hint : Acid is  $\text{HNO}_2$ )
31. Nitrous acid is considered as a factomaric mixture of two forms. Write its structures.
32.  $\text{NH}_3 + \text{O}_2 \longrightarrow \text{X} + \text{H}_2\text{O}$ ;  $\text{X} + \text{O}_2 \longrightarrow \text{Y}$ ;  $\text{Y} + \text{H}_2\text{O} \longrightarrow \text{Z} + \text{X}$  and  $\text{Z} + \text{Zn} \longrightarrow \text{Zn}(\text{NO}_3)_2 + \text{H}_2\text{O} + \text{Y}$ . What are X and Z in the above sequence of reactions? (Ans : X = NO; Z =  $\text{HNO}_3$ )
33. A colourless inorganic salt (X) decomposes at  $300^\circ\text{C}$  to give products Y and Z, leaving no residue. Z is neutral liquid oxide at room temperature and Y is a colourless diamagnetic neutral oxide. White phosphorus burns in excess Y, produce a strong dehydrating agent and most abundant gas in earths atmosphere. Write all equations related. (Hint : X is  $\text{NH}_4\text{NO}_3$ )

