

## GROUP 15 ELEMENTS : THE NITROGEN FAMILY

### General Introduction

The elements of nitrogen family, i.e., group 15 of periodic table are: Nitrogen (N), Phosphorus (P), Arsenic (As), Antimony (Sb) and Bismuth (Bi). Collectively, the group 15 elements are called 'pnictogens' and their compounds as 'pniconides'. The name is derived from Greek work 'pnicomigs' meaning 'suffocation'. In the section, we will discuss the main group trends and the Chemistry of nitrogen and phosphorus and their compounds

Group15 Elements
N
P
As
Sb
Bi

### Occurrence

**Nitrogen** : The first member of this group, i.e., Nitrogen occurs as a diatomic gas,  $N_2$ . It makes about 78% by volume of atmosphere. Despite this, it is not a very abundant element in the earth's crust. It is only the 33<sup>rd</sup> most abundant element by mass in earth's crust (~9ppm). It mainly occurs as nitrates. Since nitrates are very much soluble in water, so these are not wide-spread in earth's crust. The only major nitrates are  $NaNO_3$  (Chile saltpeter) and  $KNO_3$  (Indian Saltpeter). Nitrogen is the essential constituent of proteins, amino acids and nucleic acids which regulate the growth and control the hereditary effects in living beings.

**Phosphorous** : It is a very reactive element and hence it does not occur free in nature. However, it is the 11<sup>th</sup> most abundant element by mass in the earth's crust. It occurs in the minerals of the apatite family,  $Ca_3(PO_4)_6.CaX_2(X=F,Cl \text{ or } OH)$ , e.g.

- (a) Fluorapatite,  $3Ca_3(PO_4)_2.CaF_2$
- (b) Chloroapatite,  $3Ca_3(PO_4)_2.CaCl_2$
- (c) Hydroxyapatite,  $3Ca_3(PO_4)_2.Ca(OH)_2$

These minerals are the major components of the phosphate rocks. Large deposits of phosphate rocks are found in North Africa and North America. In India, phosphate rocks are found in Rajasthan.

**Phosphorous** : It is an essential constituent of animal and plant matter. It is present in the bones as well as in living cells. About 60% of our bones and teeth are  $Ca_3(PO_4)_2$  or fluoroapatite.

Phosphoproteins are present in milk and eggs. It also occurs in nucleic acids (DNA and RNA) which control the hereditary effects in human beings. Phosphorus is also found in ATP (adenosine triphosphate) and adenosine diphosphate (ADP) which are of vital importance for production of energy in the cells.

**Arsenic, Antimony and Bismuth**: The elements such as As, Sb and Bi are not very abundant. They mainly occur as sulphides (i.e, arsenopyrites,  $(FeAsS)$ , stibnite  $(Sb_2S_3)$  and bismuth glance  $(Bi_2S_3)$  and as traces in other ores. These are obtained as metallurgical by products from roasting sulphide ores.

### GENERAL CHARACTERISTICS OF GROUP 15 ELEMENTS :

- (a) **Electronic Configuration** : The electronic configuration of the elements of group 15 are given by Table 1.1 The general valence shell electronic configuration of the elements of group 15 is  $ns^2 np^3$ , where  $n=2$  to 6. The three electrons in p-orbitals are distributed as  $px^1, py^1, pz^1$ . In accordance with Hund's rule.

Table 1.1 Electronic Configuration of elements of Group 15

Element	Symbol	Atomic No.	Electronic 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>

The Abundance of these elements in earth's crust is given below:

Element	Abundance in earth's crust(ppm)	Relative Abundance
N	19	33
P	1120	11
As	1.8	52
Sb	0.20	64
Bi	0.008	71

**(b) Atomic and Physical Properties :** Some of the important atomic and physical properties of the elements of nitrogen family or group 15 elements are summarized in Table 1.2 Some Atomic and Physical Properties of Group 15 Elements are :

	N	P	As	Sb	Bi	
Atomic Number	7	15	33	51	83	
Atomic mass (g mol <sup>-1</sup> )	14.01	30.97	74.92	121.75	208.96	
Atomic radius covalent(pm)	70	110	121	141	148	
Ionic radius(pm)	171	212	222	76	103	
	(N <sup>3-</sup> )	(P <sup>3-</sup> )	(As <sup>3-</sup> )	Sb <sup>3+</sup>	Bi <sup>3+</sup>	
Ionisation Enthalpy (kJ mol <sup>-1</sup> )	IE <sub>1</sub>	1402	1012	947	834	703
	IE <sub>2</sub>	2856	1903	1798	1595	1610
	IE <sub>3</sub>	4577	2910	2736	2443	2466
Electronegativity	3.0	2.1	2.0	1.9	1.9	
m.p.(K)	63 (Molecular)	317.1 (White P)	1089 (Grey α-form at 38.6 atm)	904	544.4	
b.p.(K)	77.2 (Molecular)	553.5 (White P)	888 (Sublimation temp.)	1860	1837	
Density (g cm <sup>-3</sup> ) at 298 K	0.879 (at 63 K)	1.823	5.778 (Grey α-form)	6.697	9.808	

## Atomic Properties

1. **Atomic and ionic radii.** (a) *The atomic (covalent) and ionic radii (in a particular oxidation state) of the elements of nitrogen family (group 15) are smaller than the corresponding elements of carbon family (group 14).*

**Explanation:** This is because on moving from left to right, i.e., from group 14 to 15 in a given period, the nuclear charge increases while the new electron enters the small shell. Further, the electrons in the same shell do not screen each other. Therefore, the effective nuclear charge increases and hence the electrons are more strongly attracted towards the nucleus. This results in a decrease in covalent radii. Same is true for ionic radii.

(b) *On moving down the group, the covalent and ionic radii (in a particular oxidation state) increase with increase in atomic number. There is considerable increase in covalent radius from N to P. However, from As to Bi, only a small increase is observed.*

**Explanation:** Down the group, the covalent radii increase primarily due to the addition of a new principal energy shell in each succeeding element. The considerable increase in covalent radius from N to P is not only due to the addition of a new energy shell but it is also due to the strong shielding effect of the  $s$  and  $p$ -electrons present in the inner shells. However, the small increase in covalent radii from As to Bi is due to the poor shielding effect of valence electrons by the  $d$  and  $f$  electrons present in the inner shells of heavier elements. As a result, the effective nuclear charge increases which reduces the effect of addition of a new energy shell to some extent. Consequently, the increase in covalent radius is small from As to Bi. Same is true for ionic radii.

2. **Ionization Enthalpy.** *The ionization enthalpies of the elements of group 15 are much higher than those of the corresponding elements of the group 14. On going down the group, the ionization enthalpies decrease regularly.*

**Explanation :** Because of increased nuclear charge, small size and stable half filled ( $np_x^1$ ,  $np_y^1$ ,  $np_z^1$ ) electronic configurations, the valence electrons of group 15 elements are strongly attracted by the nucleus and hence they have less tendency to lose electrons. As a result, ionization enthalpies of the elements of the nitrogen family are much higher as compared to the corresponding elements of the carbon family. But the decrease in values of ionization energies as we move down the group is due to the gradual increase in the atomic size and screening effect which reduces the force of attraction on the electrons by the nucleus.

As expected, successive ionization enthalpies of these elements increase in the order

$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3 \text{ (Table 1.2)}$$

3. **Electronegativity :** *The electronegativity values of elements of group 15 are higher than the corresponding elements of group 14. On moving down the group, the electronegativity value decreases.*

**Explanation:** Due to smaller atomic size and greater nuclear charge, they have higher electronegativity value. However, the electronegativity decreases down the group due to a corresponding increase in size from N to Bi. But the decrease is not regular in heavier elements.

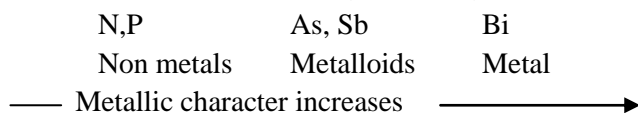
## Physical Properties

Some important properties of the elements group 15 are discussed below:

- 1. Metallic Character .** *The elements of group 15 are less metallic than the corresponding elements of group 14.*

However, on moving down the group, the metallic character increases from N to Bi.

**Explanation:** Due to increased nuclear charge and higher electronegativity, the elements of group 15 are less metallic than the corresponding elements of group 14. On moving down the group, the electronegativity decreases. As a result, valence electrons are lost more readily and hence the metallic character increases. For example: first two elements of this group (N and P) are non-metals, the next two (As and Sb) are metalloids, while Bi is a metal.



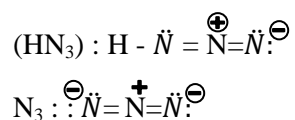
- 2. Melting and Boiling points:** *The melting points of group 15 elements first increase from N to As and then decrease to Sb and Bi. The boiling points, however, increase regularly as we move from N to Bi.*

**Explanation:** The melting points increase down the group from N to As due to increase in their atomic size. However, the unexpected decrease in the melting points of antimony and bismuth is because of their tendency to form three covalent bonds instead of five covalent bonds due to **inert pair effect**. Hence, the attraction among their atoms is weak, thereby lowering their melting points. Because of larger size of atoms, Bi has still weaker inter atomic forces than Sb and thus has still lower melting point.

The boiling points increase down the group from N to Bi due to an increase in their atomic size.

- 3. Density:** *The density of the elements of group 15 increases regularly from top to bottom, i.e., from N to Bi as usual.*
- 4. Allotropy:** Except nitrogen and bismuth, all the elements of this group show allotropy. *Phosphorus* exists in three allotropic forms, i.e., white, red and black phosphorus. *Arsenic* and *Antimony* exist in two allotropic forms, i.e., yellow and grey.

**Catenation :** The elements of this group also show a tendency to form bonds with itself known as Catenation. But all these elements show this property to a much smaller extent than carbon. For example: Hydrazoic acid ( $\text{HN}_3$ ) has three N atoms bonded together, azide ion ( $\text{N}^{3-}$ ) has also three atoms bonded together :



Among group 15 elements, phosphorus has the maximum tendency for catenation forming cyclic as well as open chain compounds.

## (c) Chemical Properties

### Oxidation States

**(i) Negative oxidation states :** All the elements of this group have five electrons in valence shell ( $ns^2np^3$ ) and thus require three more electrons to acquire the nearest noble gas configuration. Although gain of three electrons to form  $M^{-3}$  ions requires large amount of energy, yet it takes place only with nitrogen, because it is the smallest and the most electronegative element of this group. Thus, nitrogen forms  $N^{-3}$  (nitride) ion and shows an oxidation state of -3 in nitrides of some highly electropositive metals such as  $Mg_3N_2$ ,  $Ca_3N_2$  etc. Other elements of this group form covalent compounds even with metals and show an oxidation state of -3. For example, Calcium phosphide ( $Ca_3P_2$ ), Sodium Arsenide ( $Na_3As$ ), Zinc stibide ( $Zn_3Sb_2$ ) and Magnesium bismuthide ( $Mg_3Bi_2$ ). *However, the tendency of these elements to show -3 oxidation state decreases as we move down the group from N to Bi, due to increase in their size and metallic character.* In addition to -3, N and P also show oxidation states of -2 in hydrazine ( $NH_2NH_2$ ) and diphosphine  $P_2H_4$  respectively. Nitrogen also show an oxidation state of -1 in hydroxylamine ( $NH_2OH$ ) but phosphorus does not.

**(ii) Positive oxidation states:** All elements of this group show positive oxidation states of +3 and +5. However, *on moving down the group, the stability of +5 oxidation state decreases while that of +3 oxidation state increases due to inert pair effect. Thus +5 oxidation state of Bi is less stable than +5 oxidation state of Sb. The only stable compound of bismuth having +5 oxidation state is  $BiF_5$ .*

Further, due to large amount of energy needed to lose all five valence electrons,  $M^{5+}$  ions cannot be formed. In other words, all the compound of group 15 elements having +5 oxidation state (i.e. :  $PF_5$ ,  $PCl_5$ ,  $SbF_5$ ,  $BiF_5$ ) are essentially covalent. However, elements of this group form both ionic (i.e.  $BiF_3$ ,  $SbF_3$ ) and covalent compounds (i.e.  $NCl_3$ ,  $PCl_3$ ,  $AsCl_3$ ,  $SbCl_3$ ) in +3 oxidation state. The +3 oxidation state becomes more and more stable on moving down the group. This is due to inert pair effect.

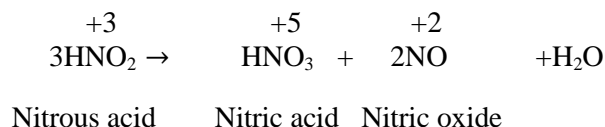
**(Inert pair Effect:** The reluctance of the s-electron pair to take part in chemical combination is called inert pair effect.)

It may, however, be pointed out here that nitrogen because of its small size, high electro negativity and strong tendency to form P- $\pi$ , p- $\pi$  multiple bonds, shows all oxidation states from -3 to +5 as shown below:

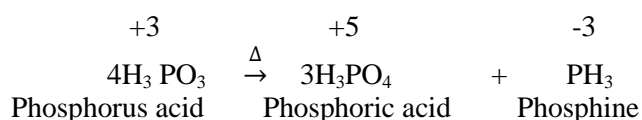
Compound	$NH_3$	$NH_2NH_2$	$NH_2OH$	$N_2$	$N_2O$	NO	$N_2O_3$	$NO_2$ or $N_2O_4$	$N_2O_5$
Oxidation State	-3	-2	-1	0	+1	+2	+3	+4	+5

**Maximum Covalency:** Since nitrogen does not possess vacant d-orbitals in its valence shell ( $n=2$ ) therefore it can show a maximum covalency of four and that too when it donates its lone pair of electrons [ $NH_4^+$ ,  $CH_3$ ],  $N^+$  etc] In other words, nitrogen cannot extend its covalency beyond 4. That is why nitrogen does not form pentahalides such as  $NF_5$  or  $NCl_5$ . On the other hand, phosphorus and all other elements have empty d-orbitals and can utilize all their valence orbitals to exhibit covalency of 5 or 6 e.g.  $PCl_5$ ,  $PF_5$ ,  $AsF_5$ ,  $[PF_6]$ ,  $[SbF_6]$ , etc.

**(iv) Disproportionation :** All the oxidation states of nitrogen from +1 to +4 show disproportionation in acidic medium. For example,



Similarly, in case of phosphorus, all the intermediate oxidation states from -3 to +5 show disproportionation both in acidic and alkali solutions. For example,



However, due to inert pair effect as the stability of +3 oxidation states increases from As to Bi, their tendency to undergo disproportionation decreases.

## Trends in chemical Reactivity

Some important trends in the chemical reactivity of some of the compounds of these elements are discussed below:

1. **Reactivity towards Hydrogen (Formation of Hydrides)** : All elements from group 15 form volatile trihydrides of the formula  $\text{EH}_3$ , where E= N,P,As, Sb, Bi.

These are named as

$\text{NH}_3$	$\text{PH}_3$	$\text{AsH}_3$	$\text{SbH}_3$	$\text{BiH}_3$
Ammonia	Phosphine	Arsine	Stibine	Bismuthine

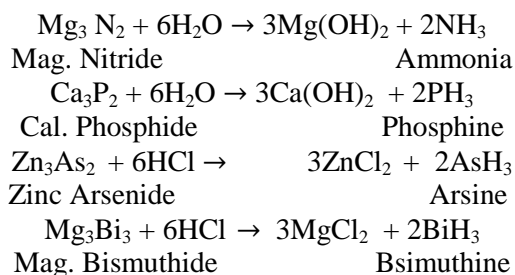
Some of properties of these hydrides are shown in Table 1.3

Table 1.3 Properties of Hydrides of Group 15 elements

Property	$\text{NH}_3$	$\text{PH}_3$	$\text{AsH}_3$	$\text{SbH}_3$	$\text{BiH}_3$
Melting point (K)	195.2	139.5	156.	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 ( $^\circ$ )	107.8	93.6	91.8	91.3	-
$\Delta_f H^\circ$ (kJ mol $^{-1}$ )	-46.1	13.4	66.4	145.1	278
$\Delta_{\text{diss}} H^\circ$ (E-H) (kJ mol $^{-1}$ )	389	322	247	255	-

The lighter elements also form hydrides of the formula  $\text{E}_2\text{H}_4$  such as  $\text{N}_2\text{H}_4$  (hydrazine),  $\text{P}_2\text{H}_4$  (diphosphine) and  $\text{As}_2\text{H}_4$  (diarsine). Nitrogen also forms a special hydride of the formula  $\text{HN}_3$ , it is called hydrazoic acid.

**Preparation (i) By hydrolysis of binary metal compounds:** The Hydrides of group 15 are prepared from their corresponding binary metal compounds such as  $\text{Mg}_3\text{N}_2$ ,  $\text{Ca}_3\text{P}_2$ ,  $\text{Zn}_3\text{As}_2$  or  $\text{Mg}_3\text{Bi}_2$  by hydrolysis with water or dilute acids. Thus,



(ii) **By reduction of trichlorides :** The trichlorides of these elements except that of bismuth upon reduction with Zinc/Acid or  $\text{LiAlH}_4$  give the corresponding hydrides.



**Ammonia ( $\text{NH}_3$ )** is the most important trihalide of the group and is extensively used in the manufacture of nitric acid ( $\text{HNO}_3$ ) and important chemical fertilizers such as urea, ammonium sulphate, calcium cyanamide etc. It is prepared on an industrial scale by Haber's process as discussed later on.

**Structure:** All these elements undergo  $\text{Sp}^3$  hybridization and have pyramidal structure. These are covalent in nature. The structure of  $\text{NH}_3$  molecule is shown in figure(4). Here, due to presence of lone pair, the bond angle in  $\text{NH}_3$  is less than normal tetrahedral angle, it is found to be  $107^\circ$ . As we go down the group bond angle decreases as:

$\text{NH}_3$	$\text{PH}_3$	$\text{AsH}_3$	$\text{SbH}_3$	$\text{BiH}_3$
$107.8^\circ$	$93.6^\circ$	$91.8^\circ$	$91.3^\circ$	$90^\circ$

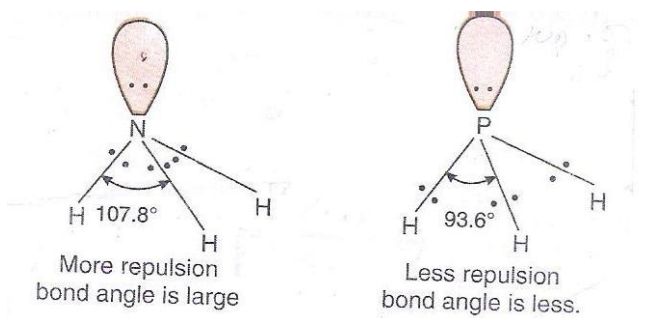


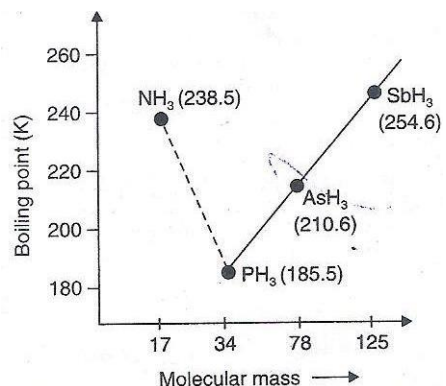
Fig (4)

**Repulsions between electron pairs in  $\text{NH}_3$  and  $\text{PH}_3$**

**Explanation:** This decrease in bond angles can be explained on the basis of the size and electronegativity of the central atom. As we move down the group, the size of central atom goes on increasing & its electronegativity goes on decreasing. As a result, the bond pairs of the electrons tends to lie away and away from the central atom in moving from  $\text{NH}_3$  to  $\text{BiH}_3$ . In other words, the force of repulsion between the adjacent bond pairs is maximum in  $\text{NH}_3$  and minimum in  $\text{BiH}_3$ . Consequently, the bond angle is maximum in  $\text{NH}_3$  and minimum in  $\text{BiH}_3$ .

**Main Properties of Hydrides:**

- (i) **Boiling Points :** Ammonia has a higher boiling point than phosphine and then the boiling point increases down the group because of increase in size as shown below in (fig5)



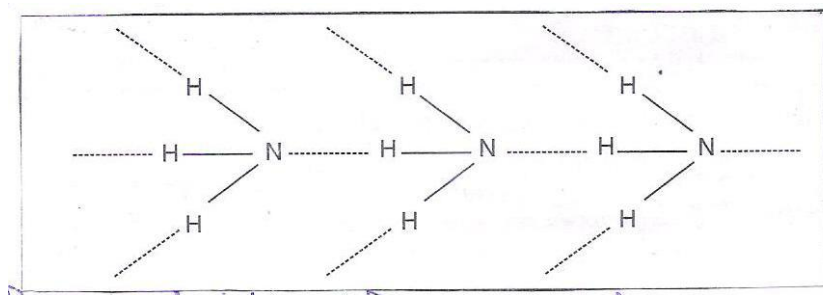
Fig(5)

### Plot of boiling Points of the hydrides of group 15 elements

Molecule	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	BiH <sub>3</sub>
Boiling Point (K)	238.5	185.5	210.6	254.6	290
Melting Point(K)	195.2	139.5	156.7	185.0	-

Similar behaviour is observed for melting points

**Explanation:** The abnormally high boiling point of ammonia is due to its tendency to form hydrogen bonds. The electronegativity of N (3.0) is much higher than that of H (2.1), as a result N-H bonds are polar and therefore, NH<sub>3</sub> undergo intermolecular hydrogen bonding as shown below in fig(6):



Fig(6)

In PH<sub>3</sub> and other hydrides, the intermolecular forces are vander waals forces. These vander waals forces increase with increase in molecular size and therefore, boiling points increase on moving from PH<sub>3</sub> to BiH<sub>3</sub>. In contrast, the electronegativities of P(2.1), As (2.0), Sb (1.9) and Bi (1.9) are close to H (2.1) and hence PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub> and BiH<sub>3</sub> do not form H-bonds. Thus, abnormally high b.p of NH<sub>3</sub> is due to intermolecular H-bonding.

Further, as we move from PH<sub>3</sub> to BiH<sub>3</sub>, the molecular mass increases. As a result, *the vander waals forces of attraction* increase and the boiling points increase regularly from PH<sub>3</sub> to BiH<sub>3</sub>. However, *the b.p. of NH<sub>3</sub> is higher than those of PH<sub>3</sub> and AsH<sub>3</sub> but lower than those of SbH<sub>3</sub> and BiH<sub>3</sub>. This is probably due to the reason that the increase in boiling points of SbH<sub>3</sub> and BiH<sub>3</sub> because of higher van der waals forces of attraction is more than the increase in b.p. of NH<sub>3</sub> because of H-bonding.* Thus, in a nutshell, the boiling points of hydrides of group 15 elements follow the order :





- (ii) **Melting Points:** Because of intermolecular H-bonding,  $\text{NH}_3$  has the highest melting point. The other hydrides of this group do not form H-bonds and hence their melting points are lower than that of  $\text{NH}_3$ . However, as we move down the group from  $\text{PH}_3$  to  $\text{SbH}_3$ , the molecular size increases and hence the melting points increase regularly due to a corresponding increase in their Vander Waals forces of attraction. Thus, the melting points of the hydrides of group 15 elements follow the sequence :
- (iii) **Solubility:** Ammonia forms hydrogen bonding with water molecules while phosphine and other hydrides do not form hydrogen bonding with water. Therefore,  $\text{NH}_3$  is soluble in water while  $\text{PH}_3$  and other hydrides are insoluble in water
- (iv) **Basic Strength:** All these hydrides have one lone pair of electrons on their central atom. Therefore, they act as Lewis base. They can donate an electron pair to electron deficient species (Lewis acids). As we go down the group, the basic character of these hydrides decreases. For example,  $\text{NH}_3$  is distinctly basic;  $\text{PH}_3$  is weakly basic;  $\text{AsH}_3$ ,  $\text{SbH}_3$  and  $\text{BiH}_3$  are not basic at all.

**Explanation :** Nitrogen atom has the smallest size among the hydrides. Therefore, the lone pair is concentrated on a small region and electron density on it is the maximum consequently, its electron releasing tendency is maximum. As the size of the central atom increases down the family, the electron density also decreases. As a result, the electron donor capacity or the basic strength decreases down the group.

- (v) **Thermal Stability :** Thermal stability of the hydrides of group 15 elements decreases as we go down the group. Therefore,  $\text{NH}_3$  is most stable and  $\text{BiH}_3$  is least stable. The stability of the hydrides of group 15 elements decreases in the order :

**$\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$**

**Explanation** This is due to the fact that on going down the group the size of the central atom increases and therefore, its tendency to form stable covalent bond with small hydrogen atom decreases. As a result the M-H bond strength decreases and therefore thermal stability decreases :

- (vi) **Reducing Character :** The reducing character of the hydrides of group 15 elements increases from  $\text{NH}_3$  to  $\text{BiH}_3$ . Thus, increasing order of reducing character is as follows :  
 $\text{NH}_3$
- (vii) **Explanation :** the reducing character depends upon the stability of the hydride. The greater is the instability of a hydride, the greater is its reducing character. Since the stability of group 15 hydrides decreases from  $\text{NH}_3$  to  $\text{BiH}_3$ , hence the reducing character increases. For example,  $\text{NH}_3$  being most stable among the group 15 hydrides is not a good reducing agent. The other hydrides being unstable act as good reducing agents. However it may be noted that ammonia at high temperature reduces copper oxide to copper :  

$$3\text{CuO} + 2\text{NH}_3 \xrightarrow{\text{heat}} 3\text{Cu} + \text{N}_2 + 3\text{H}_2\text{O}$$

2. **Reactivity towards oxygen (Formation of Oxides)** Nitrogen has a strong tendency to form  $\text{P}\pi\text{-P}\pi$  multiple bonds between N and O atoms, whereas other elements of this group have not. Consequently N forms a number of oxides which have no P, As, Sb or Bi analogues. Actually nitrogen forms five oxides with oxidation states ranging from +1 to +5 while other elements form oxides only in +3 and +5 oxidation states as shown in table 1.4

**Table 1.4 Oxides of Group 15 elements**

Oxidation state	Oxides of Nitrogen	Oxides of Phosphorus	Oxides of Arsenic	Oxides of antimony	Oxides of Bismuth
+1	N <sub>2</sub> O Nitrous Oxide	-	-	-	-
+2	NO Nitric Oxide	-	-	-	-
+3	N <sub>2</sub> O <sub>3</sub> <b>Dinitrogen trioxide</b>	P <sub>4</sub> O <sub>6</sub> Phosphorus trioxide	As <sub>4</sub> O <sub>6</sub> Arsenic trioxide	Sb <sub>4</sub> O <sub>6</sub>	Bi <sub>2</sub> O <sub>3</sub>
+4	N <sub>2</sub> O <sub>4</sub> <b>Dinitrogen tetroxide</b> or NO <sub>2</sub>	P <sub>4</sub> O <sub>8</sub> Phosphorus tetroxide	-	-	-
+5	N <sub>2</sub> O <sub>5</sub> <b>Dinitrogen pentoxide</b>	P <sub>4</sub> O <sub>10</sub> Ph			

In general, oxides of non –metals are acidic, those of metalloids are amphoteric while those of metals are basic. Further, greater the electronegativity of the element, more acidic is the oxide. Among the oxides of the same element, higher the oxidation state of the element, more is its acidic strength. Keeping above facts in mind, the following conclusions can be drawn about acidic character of oxides of group 15 elements.

- (i) Acidic strength of oxides of nitrogen increases in the order :  
N<sub>2</sub>O/ NO . N<sub>2</sub>O<sub>3</sub> / N<sub>2</sub>O<sub>4</sub> N<sub>2</sub>O<sub>5</sub> ; N<sub>2</sub>O and NO are, however, neutral
- (ii) Acidic strength of trioxides follows the order : N<sub>2</sub>O<sub>3</sub> > P<sub>4</sub>.....
- (iii) Acidic strength of pentoxides follows the order : .....

3. **Reactivity towards Halogens (Formation of Halides)** The elements of group 15 form two types of halides, viz, trihalides and pentahalides. The trihalides are formed by all the elements while pentahalides are formed by all the elements except nitrogen. Nitrogen cannot form pentahalides due to the absence of vacant d-orbitals in the outermost shell. Similarly, the last element; Bi has little tendency to form pentahalides because +5 oxidation state of Bi is less stable than +3 oxidation state due to inert pair effect.

- (a) **Trihalides** : All the elements of group 15 form trihalides of the general formula, E<sub>3</sub>X<sub>3</sub>. All these trihalides (E=N, P, As, Sb or Bi and X=F, Cl, Br or I) are known.

**Structure** : Like ammonia, trihalides have pyramidal structures i.e., the central element is sp<sup>3</sup>-hybridized. Three of the four sp<sup>3</sup> – orbitals form bonds with halogen atoms while the fourth sp<sup>3</sup>-orbital contains the lone pair of electrons (fig 7)

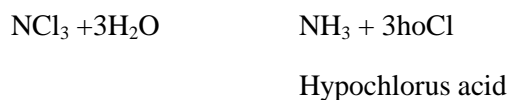
Properties (i) these Trihalides are predominally covalent with the ionic character increasing down the group. Thus,  $\text{Bf}_3$  is predominately ionic while other halides of Bi, i.e.,  $\text{BiCl}_3$ ,  $\text{BiBr}_3$ , etc and  $\text{SbF}_3$  are partly covalent and partly ionic

(ii) Out of the trihalides, trihalides of N are less stable  $\text{NF}_3$  is however, stable.  $\text{NCl}_3$  is explosive while  $\text{NBr}_3$  and  $\text{NI}_3$  are known only as their unstable ammoniates, i.e.,  $\text{NBr}_3 \cdot \text{NH}_3$  and  $\text{NI}_3 \cdot \text{NH}_3$ , where  $\text{NBr}_3$  explodes even at 173K. the nitrogen triiodide ammoniate is stable only in the moist state In the dry state, it explodes with noise when struck liberating vapours of  $\text{I}_2$ . Thus, it is a mild and harmless explosive.

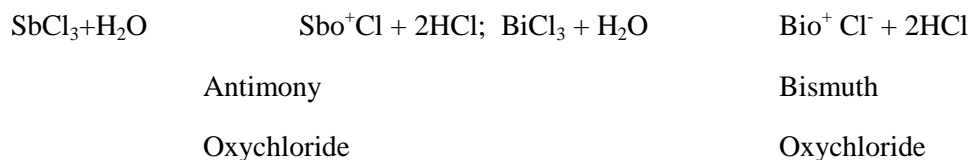


The instability of  $\text{NCl}_3$ ,  $\text{NBr}_3$  and  $\text{NI}_3$  is because of the weakness of N-X bond due to large difference in the size of N and X atoms However, the difference in the size of N (75pm) and F (72pm) is small, N-F bond is quite strong. As a result,  $\text{NF}_3$  is an exothermic compound So, it is quite stable and does not undergo hydrolysis with water, dilute acids or alkalis.

(iii) The trihalides readily undergo hydrolysis but the products are different in different hydrolytic reactions For Example :



In contrast the trichlorides of Bi and Sb are only partially and reversibly hydrolysed to give oxychloride of the corresponding metal, i.e.,

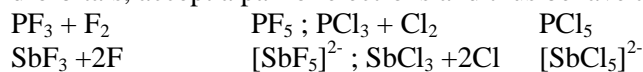


In accordance with Le Chatelier principle, the addition of excess of HCl suppresses the hydrolysis by shifting the equilibrium to the left.

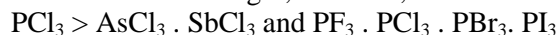
From the above discussion, it follows that the ease of hydrolysis of trihalides follows the order :



(iv) The trihalides of P, As and Sb (especially the fluorides and chlorides) due to the presence of d-orbitals, accept a pair of electrons and thus behave as Lewis acids.



The Lewis acid strength, however, decrease in the order :



In contrast, the trihalides of nitrogen due to absence of d-orbitals and presence of a lone pair of electrons, behave as Lewis bases. However,  $\text{NF}_3$  has a little tendency to donate a pair of electrons because of high electronegativity of F. The Lewis base strength of other trihalides increases as the electronegativity of Halogen decreases, i.e.,  $\text{NF}_3$ ..... Because, less electronegative halide ion cannot pull the electrons towards itself and they are free for donation.

- (b) **Pentahalides:** P, As Sb form pentahalides of the general formula  $\text{EX}_5$  due to presence of vacant d-orbitals in their respective valence shells. N does not form pentahalides due to the absence of d-orbitals in its valence shell.

Actually, pentahalides are thermally less stable than trihalides because of following two reasons:

- (i) As we move down the group, the stability of +3 oxidation state increases while that of +5 oxidation state decreases due to inert pair effect.
- (ii) As the size of the halogen increases from F to I, the strength of the E-X bond decreases and the steric hindrance increases. The combined effect of these two factors makes pentabromides unstable. Therefore, the pentahalides of group 15 are less in number as compared to trihalides. For example, pentafluorides of P, As, Sb and Bi are all known, pentabromide of only phosphorus, i.e.,  $\text{PBr}_5$  is known while pentaiodides of none of these elements is stable. In other words, Bi forms only pentafluoride.

**Preparation :** The pentahalides are prepared as follows:



**Structure :** All the pentahalides have trigonal *bipyramid geometry*, i.e., the central atom is  $\text{Sp}^3$  hybridized. The three halogen atoms occupy equatorial positions while the other two occupy axial positions. Since the three equatorial E-X bonds are repelled by two electron pairs but the two axial E-X bonds are repelled by three electron pairs, therefore, axial bonds are usually longer than the equatorial bonds. The axial bonds are at  $90^\circ$  while equatorial bonds are at  $120^\circ$  each. The structure of pentahalides is illustrated by the structure of  $\text{PF}_5$  as shown in fig 7(b)

Fig 8 Structure  $\text{P}_4$  molecule

**Properties :** (i) Pentahalides are thermally less stable than their corresponding trihalides, i.e.,  $\text{PCl}_5$   $\text{PCl}_3 + \text{Cl}_2$ . That is why corresponding trihalides, i.e.,  $\text{PCl}_5$  behave as a good chlorinating agent.

$\text{PCl}_5$  is covalent in the vapour state but exists as  $[\text{PCl}_4]^+[\text{PCl}_6]^-$  in the crystalline state. In the solid state,  $\text{PBr}_5$  exists as  $[\text{PBr}_4]^+ \text{Br}^-$  while  $\text{PCl}_5$  exists as  $[\text{Pl}_4]^+ \text{I}^-$  in solution.

(ii) All the pentahalides act as Lewis acids due to the presence of vacant orbitals, the central atom (except) can accept a pair of electrons thereby expanding its co-ordination number to 6, i.e.,  $\text{X} \dots \dots \dots$

As a result, the hybridization of the central atom changes from  $\text{sp}^3\text{d}$  to  $\text{sp}^3\text{d}^2$ .

(iii)  $\text{PF}_5$  does not undergo hydrolysis since P-F bond is stronger. All other pentahalides of P, however, undergo hydrolysis to yield  $\text{H}_3\text{PO}_4$ .

**4. Reactivity towards Metals (Formation of Binary Compounds)** All the elements of group 15 form binary compounds with metals in the +3 oxidation state. For example  $\text{Ca}_3\text{N}_2$  (Calcium nitride),  $\text{Ca}_3\text{P}_2$  (Calcium phosphide),  $\text{Na}_3\text{As}_2$  (sodium arsenide),  $\text{Zn}_3\text{Sb}_2$  (zinc stibide) and  $\text{Mg}_3\text{Bi}_2$  (magnesium bismuthide).

### 1.1 Anomalous Properties of Nitrogen

Nitrogen, the first member of group 15 elements, shows anomalous behavior and differs from the rest of the members of its family. The main reasons for this are as follows:

- (i) *Small atomic size*
- (ii) *High ionisation enthalpy*
- (iii) *High electronegativity*
- (iv) *Absence of d-orbitals in the valence shell*

Some important properties in which nitrogen differs from the rest of the members of its group are as follows:

1.  $\text{p}\pi\text{-p}\pi$  multiple bonds: Nitrogen because of its small size and high electronegativity forms  $\text{p}\pi\text{-p}\pi$  multiple bonds with itself and with other elements having small size and high electronegativity. Nitrogen molecule has a triple bond (N  $\dots\dots$  N, one  $\sigma$  bond and two  $\pi$  bonds) between the two atoms. These  $\text{N}_2$  molecules are held together by weak *vander waals forces of attraction* which can be easily broken by the collisions of the molecules at room temperature. Therefore,  $\text{N}_2$  is a gas at room temperature.

The other elements of this group do not form  $\text{p}\pi\text{-p}\pi$  multiple bonds because their atomic orbitals are so large and diffused that they cannot have effective overlapping.