Inorganic chemistry II
Second stage / Second semester
Sixth lecture 2021/2022 Pro. Dr. Mohammed Hamid

Elements of Group VA or 15
(Elements of Nitrogen and Phosphorus Family, ns^2np^3)

POSITION IN PERIODIC TABLE

VA group or 15th group of the extended form of the periodic table consists of six elements nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi) and ununpentium (Uup)*. This group of six elements constitutes a family. These elements are collectively known as pnictogens. These are *p*-block elements as he last differentiating electron is accommodated on *np* shell. These elements have five electrons in the valency shell. The elements of the group possess the same electronic configuration and show similarities as well as gradation in their properties with rise of atomic number from nitrogen to ununpentium. Thus, their inclusion in the same group is justified on the basis of electronic configuration and physical and chemical properties which are given below:

1- Electronic Configuration : The distribution of electrons in various energy shells of the atoms of these elements is given below:

Element	At.NO.	Electronic configuration	Inert gas core
N	7	$1s^2 2s^2 2P^3$	[He]$2s^2 2P^3$
P	15	$1s^2 2s^2 2P^6 3s^2 3P^3$	[Ne]$3s^2 3P^3$
As	33	$1s^2 2s^2 2P^6 3s^2 3P^6 3d^{10} 4s^2 4P^3$	[Ar]$3d^{10} 4s^2 4P^3$
Sb	51	$1s^2 2s^2 2P^6 3s^2 3P^6 3d^{10} 4s^2 4P^6 4d^{10} 5s^2 5P^3$	[Kr]$4d^{10} 5s^2 5P^3$
Bi	83	$1s^2 2s^2 2P^6 3s^2 3P^6 3d^{10} 4s^2 4P^6 4d^{10}\ 4f^{14}\ 5s^2\ 5P^6\ 5d^{10}\ 6s^2\ 6P^3$	[Xe]$4f^{14} 5d^{10} 6s^2\ 6P^3$
Uup	115	$1s^2 2s^2 2P^6 3s^2 3P^6 3d^{10} 4s^2 4P^6 4d^{10}\ 4f^{14}\ 5s^2\ 5P^6 5f^{14}\ 5d^{10}\ 6s^2\ 6P^6 6d^{10} 7s^2\ 7P^3$	[Rn]$5f^{14} 6d^{10} 7s^2\ 7P^3$

Unmpentium (115) has recently been discovered it is a synthetic element. It is radioactive and is unstable in nature. Very little is known about its properties.

The configurations show that these elements have same number of electrons in the valency shell, i.e. 5 electrons in the valency shell, two of which are in *s*-orbital and remaining three in three *p*-orbitals. Thus, they have $ns^2\ np^3$ configuration, i.e., *s*-orbital is paired and three *p*-orbitals are unpaired.

The penultimate shell, in nitrogen contains 2 electrons (saturated), in phosphorus contains 8 electrons (saturated), in arsenic contains 18 electrons (saturated) while in antimony and bismuth contain 18 electrons (unsaturated) each. This shows why nitrogen differs from phosphorus in some respects and these two differ from the remaining elements of this group.

In accordance with the Hund's rule, electronic configurations involving fully filled or exactly half filled orbitals are the most stable, the elements of group VA, having exactly half filled orbitals, are also fairly stable and not so reactive. Nitrogen behaves as a noble element under ordinary conditions.

2- Similarities and gradation in physical properties :

(a) Metallic and non-metallic character : Metallic nature increases as the atomic number increases. N and P are purely non-metals while Sb and Bi are metals. Arsenic behaves as a metalloid.

$$\underbrace{\text{N}\qquad\qquad\text{P}}_{\text{Non-metals}}\qquad\underset{\text{Metalloid}}{\text{As}}\qquad\underbrace{\text{Sb}\qquad\qquad\text{Bi}}_{\text{Metals}}$$

$$\xrightarrow[\text{Metallic nature increases}]{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

N and P combine with electropositive elements and form nitrides and phosphides, respectively. Nitrides are more stable than phosphides. Bi and Sb form alloys with other metals.

(b) Physical state: There is a gradual change in physical state of these elements under ordinary conditions. Nitrogen, the first element, is a gas while phosphorus, the second member, though a solid, can pass readily into vapour state. It is soft waxy solid. The remaining elements are solids. These are hard and possess metallic lustre.

(c) Atomic radii : The atomic radii of the elements of group 15 are smaller as compared to the elements of group 14 in the corresponding periods.

$$\underset{(70\text{ pm})}{\text{N}} < \underset{(77\text{ pm})}{\text{C}} \;;\; \underset{(110\text{ pm})}{\text{P}} < \underset{(118\text{ pm})}{\text{Si}} \;;\; \underset{(121\text{ pm})}{\text{As}} < \underset{(122\text{ pm})}{\text{Ge}}$$

This is due to increased effective nuclear charge which brings contraction in size.

Atomic radii increase on going down the group.

Element	N	P	As	Sb	Bi
Atomic radii (pm)	70	110	121	141	148

The increase is due to addition of a new energy shell in each succeeding element.

There is considerable increase in covalent radius from N to P but from As to Bi only a small increase is observed.

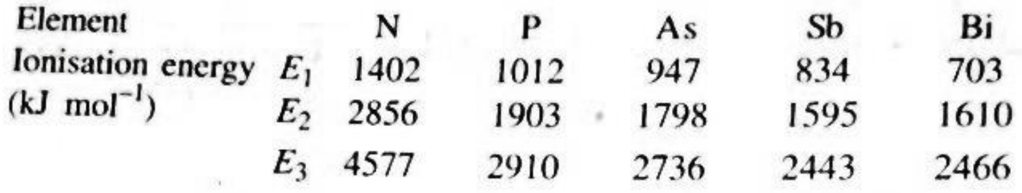
The considerable increase in covalent radius from N to P can be attributed to strong shielding effect of *s*- and *p*- electrons present in the inner shells. Small increase in covalent radii from As to Bi is, however, due to poor shielding effect of *d*- and/or *f*-electrons present in the inner shells on valency electrons. This brings increase in effective nuclear charge which reduces the effect of the addition of a new energy shell to some extent.

(d) Ionisation energy or Ionisation enthalpy: The values of first ionisation energy are higher than the corresponding group 14 elements. However, the values gradually decrease on going down the group from nitrogen to bismuth.

On account of increased nuclear charge, reduced atomic radii and stable half filled configurations, it is more difficult to remove an electron as it is more tightly held by the nucleus. Subsequently, the values of ionisation energy of these elements are higher than the elements of group 14. The decrease in the values of ionisation energy from nitrogen to bismuth is due to gradual increase in atomic size.

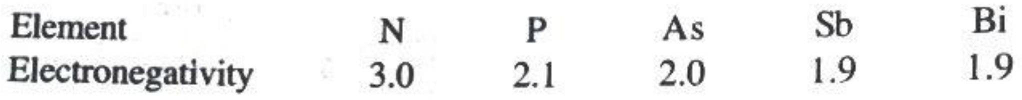
The ionisation energy of nitrogen is very high; this is due to its small size. The difference between N and P is comparatively high but the difference afterwards between two consecutive members is small. This is due to less shielding effect of *d*-electrons in As and Sb, *d*- and *f*-electrons in Bi.

Successive ionisation energies of these elements increase as expected, i.e., $E_1 < E_2 < E_3$.



Element		N	P	As	Sb	Bi
Ionisation energy ($kJ\ mol^{-1}$)	E_1	1402	1012	947	834	703
	E_2	2856	1903	1798	1595	1610
	E_3	4577	2910	2736	2443	2466

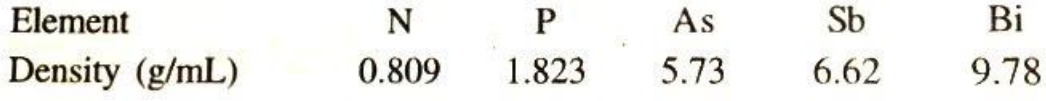
(e) Electronegativity: Electronegativity decreases gradually on descending the group from N to Bi.



Element	N	P	As	Sb	Bi
Electronegativity	3.0	2.1	2.0	1.9	1.9

Nit-rogen is most electronegative element, i.e., typical nonmetal.

(f) Density : It increases gradually on descending the group



Element	N	P	As	Sb	Bi
Density (g/mL)	0.809	1.823	5.73	6.62	9.78

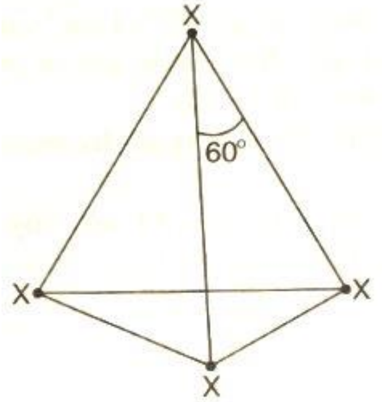
(g) Allotropy : All the elements except bismuth show allotropy. Nitrogen exists in two solid allotropic forms, α-nitrogen with cubic crystalline structure and β-nitrogen with hexagonal crystalline structure. The transition temperature is -238.5°C. Phosphorus exists in number of allotropic forms such as white, red, scarlet, α-black, β-black and violet. Arsenic is known in three allotropic forms, i.e., grey, yellow and black. Antimony also exists in three forms, i.e., yellow, black and explosive.

(h) Catenation : N, P and As exhibit the property of catenation but this property is much less than IVA elements. No nitrogen compound containing nitrogen chain with more than two atoms is stable although compounds having a chain of eight nitrogen atoms have been prepared, The bond energies of C-C, N-N,P-P and As-As linkages are 85.0, 48.0, 39.0 and 35.0 kcal/mol. Thus, the tendency of catenation decreases from N to P and from P to As. P and As can form a chain of only two atoms.

(i) Atomicity : Nitrogen is diatomic gaseous molecule at ordinary temperature. The existence of nitrogen as diatomic molecule is due to its ability to form multiple bonds. The molecule has one sigma and two π-bonds.

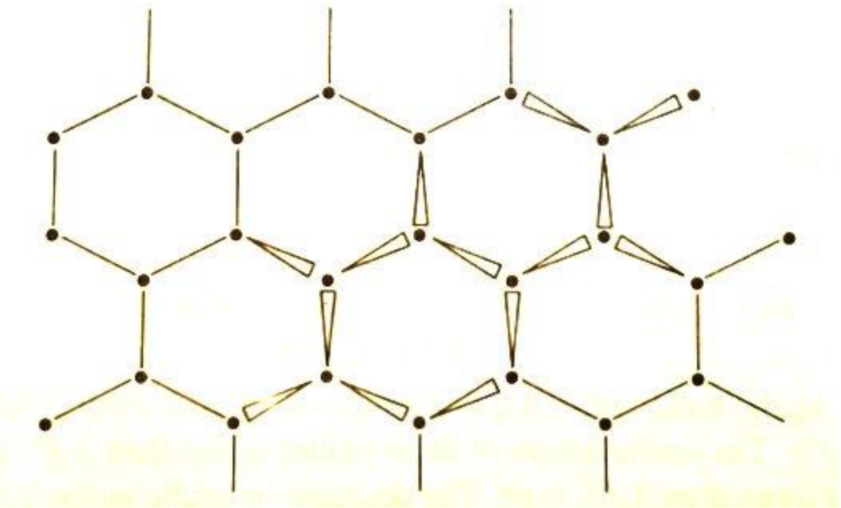
$$:N\vdots\vdots N: \quad \text{or} \quad :N\equiv N: \quad (N_2)$$

The triple bond in nitrogen molecule is very stable as the dissociation energy is very high (225 kcal/mol). It is, therefore, inert under ordinary conditions.



X= P , As, or Sb

Phosphorus, arsenic and antimony all exist as discrete tetratomic tetrahedral molecules, viz., P_4, As_4 and Sb_4 (Fig. above) as these are not capable of forming multiple bonds due to repulsion between non-bonded electrons of the inner core. The angle between X-X-X is 60°. The *pπ-pπ* bonding in phosphorus, arsenic, etc., is therefore not possible. Elements of this group form giant lattice in which bonding changes from covalent to metallic, e.g., violet and red phosphorus has layer structure involving covalent bonding. Bismuth on the other hand involves purely metallic bonding. Metallic layer structure of bismuth is given below:



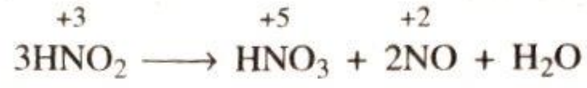
(j) Oxidation states : The elements of this group have five electrons in their outer shell. They exhibit a maximum oxidation state of +5 towards oxygen by using all the five electrons of outer shell. The tendency of the pair of *ns* electrons to remain inert (the inert pair effect) increases with increase of atomic number. Thus, only the *p*-electrons are used in bonding, i.e., +3 oxidation state is observed. +3 and +5 oxidation states of these elements are observed with halogens and sulphur. The stability of +3 oxidation state increases and that of +5 oxidation state decreases on moving down from N to Bi.

Nitrogen and phosphorus generally exhibit -3 oxidation state due to high electronegativity and small size. Nitrogen forms nitride ion (N^{3-}) with highly electropositive elements. Phosphorus also forms phosphide ion (P^{3-}) to some extent. The tendency to show -3 oxidation state decreases from nitrogen to bismuth.

Note: Nitrogen besides -3, +3 and +5 oxidation states, exhibits a large number of oxidation states from -3 to +5; -3 in NH_3 and nitrides (Li_3N, Ca_3N_2, AlN), -2 in NH_2NH_2, -1 in NH_2OH, 0 in N_2, +1 in N_2O , +2 in NO , +3 in N_2O_3 and HNO_2, +4 in NO_2, and +5 in HNO_3 and N_2O_5.

Disproportionation: All the oxidation states of nitrogen from +1 to +4 show disproportionation in acidic medium.

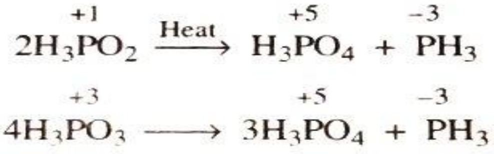
For example,



$$\overset{+3}{3HNO_2} \longrightarrow \overset{+5}{HNO_3} + \overset{+2}{2NO} + H_2O$$

Phosphorus exhibits disproportionation in all the intermediate oxidation states from -3 to +5 in acidic and basic mediums.

For example,



$$\overset{+1}{2H_3PO_2} \xrightarrow{\text{Heat}} \overset{+5}{H_3PO_4} + \overset{-3}{PH_3}$$

$$\overset{+3}{4H_3PO_3} \longrightarrow \overset{+5}{3H_3PO_4} + \overset{-3}{PH_3}$$

This tendency decreases from As to Bi due to inert pair effect as stability of +3 state increases from As to Bi.

(k) Valency and nature of bonding : There are five electrons present in the valence shell of these elements . To achieve stable configuration , they require three more electrons which is not easy to accept as to form trinegative ion (M^{3-}) due to energy considerations . Such an ion is formed by nitrogen which is smallest and most electronegative element of the family when it combines with highly electropositive metals . This tendency is much less in phosphorus . These elements easily attain stable configuration by sharing three *p*- electrons , i.e. , by forming three covalent bonds . Except nitrogen , all other elements have *d*-orbitals in the valence shell . As a result , one of the two *ns*- electrons may be promoted to *nd*- orbitals to have five unpaired orbitals in the valence shell. These can be used to form five covalent bonds . This is not possible in nitrogen as it has no *d*-orbitals (nitrogen never shows penta- valency). However , nitrogen can show a maximum covalency of 4 when it donates the *ns*- electron pair to Lewis acids .

Sb and Bi can lose three electrons forming M^{3+} ions but ionisation energy is too high for the other elements . Both SbF_3, and BiF_3 , exist as ionic solids . The M^{3+} ions are not very stable in solution . They can exist in fairly strong acid solution but are rapidly hydrolysed in water to give the antimony oxide ion or bismuth oxide ion , SbO^+ and BiO^+ . The change is reversed by adding 5M HCl

$$Bi^{3+} \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} \underset{\text{Bismuthyl ion}}{[BiO]^+} + 2H^+$$

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$

$$Sb^{3+} + H_2O \rightleftharpoons \underset{\text{Antimonyl ion}}{[SbO]^+} + 2H^+$$

Multiple bonding : Nitrogen forms *p_π- p_π* multiple bonds easily with itself and also with carbon and oxygen . Nitrogen exists as triply bonded diatomic gaseous molecule ($N \equiv N$) at ordinary temperature . The bond strength is very high (941.4 kJ mol^{-1}) and this is responsible for its inertness at ordinary conditions . Other members show reluctance to form multiple bonds . However , phosphorus can form p_π - d_π type multiple bonds , e.g. , $O = PX_3$, $RN = PX_3$.

Maximum covalency : The maximum covalency of nitrogen is four as it does not possess *d*-orbitals in the valence shell , i.e. , it cannot extend its valency beyond four [NH_4^+ , R_4N^+]. On the other hand , other members have empty *d*-orbitals and can utilise these orbitals to show covalency of five or six , e.g. , $PC1_5$, [SbF_6]$^{-1}$.

(1) Thermal and electrical conductivity : Both these properties increase on moving down the group because delocalization of electrons increases from nitrogen to bismuth .

N, P	As	Sb, Bi
Poor conductor	Semiconductor	Good conductor

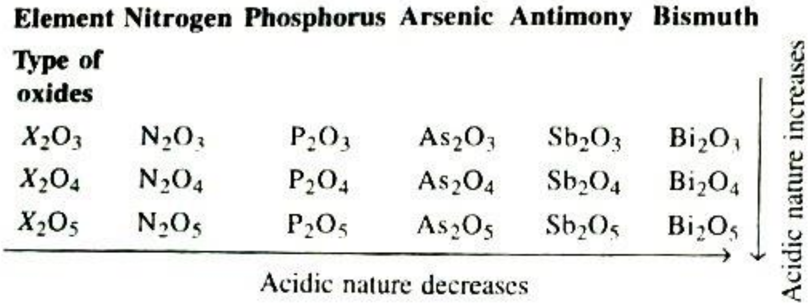
3. Occurrence : Nitrogen is found in free as well as in combined state . Nitrogen forms 75% by mass and 78% by volume of the atmosphere . In the combined state , it occurs as nitrates , proteins , amino acids , etc. Phosphorus does not occur free in nature . Phosphorus is the eleventh most abundant element in the earth's crust . Phosphorus is essential for life of both plants and animals . About 60% of bones and teeth are $Ca_3(PO_4)_2$ or $[3\{Ca_3(PO_4)_2\} .CaF_2]$

and an average person has 3.5 kg of calcium phosphate in his body . Phosphorus is present , in DNA , RNA , ATP , ADP , etc. It is also found as phosphates in nature . As , Sb and Bi are not abundant . They occur as sulphides or oxides .

4- Chemical properties : Elements of this group differ from one another appreciably in their chemical activity . Nitrogen is chemically inert under ordinary conditions . Due to this reason, it is found free in atmosphere. The chemical inertness is due to high stability of the triple bond between the two nitrogen atoms . The dissociation energy of the bond is high , i.e. , 225 kcal per mole . It is , therefore , at high temperature only when nitrogen can react with other elements .

Phosphorus especially white form is extremely reactive . It readily burns in oxygen to form oxides . The strained structure of P_4 is responsible for high chemical activity. The heavier elements are less reactive as they bum only when heated in air or oxygen to form oxides

(a) Oxides : All these elements form oxides of the type X_2O_3 ,X_2O_4 and X_3O_5.



Element Type of oxides	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
X_2O_3	N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
X_2O_4	N_2O_4	P_2O_4	As_2O_4	Sb_2O_4	Bi_2O_4
X_2O_5	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5

Greater is the electronegativity more is the acidic character of its oxide. Moreover, among the oxides of same element higher oxidation state is responsible for greater acidic character.

Besides these three types of oxides, nitrogen forms two more oxides N_2O and NO(these are neutral) and bismuth forms bismuth monoxide (BiO).

(i) Acidic nature of each type decreases from nitrogen to bismuth .

N_2O_3 and P_2O_3 are acidic , As_2O_3 and Sb_2O_3 are amphoteric while Bi_2O_3 is more basic and less acidic .

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \text{ (Nitrous acid)} \rightarrow \text{acidic}$$

$$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3 \text{ (Phosphorus acid)} \rightarrow \text{acidic}$$

$$\left.\begin{array}{l} As_2O_3 + 6HCl \longrightarrow 2AsCl_3 + 3H_2O \rightarrow \text{basic} \\ As_2O_3 + 6NaOH \longrightarrow 2Na_3AsO_3 + 3H_2O \rightarrow \text{acidic} \end{array}\right\}\text{amphoteric}$$

$$\left.\begin{array}{l} Sb_2O_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2O \rightarrow \text{basic} \\ Sb_2O_3 + 6NaOH \longrightarrow 2Na_3SbO_3 + 3H_2O \rightarrow \text{acidic} \end{array}\right\}\text{amphoteric}$$

$$Bi_2O_3 + 6HCl \longrightarrow 2BiCl_3 + 3H_2O \rightarrow \text{basic}$$

Bi_2O_3 shows feeble acidic character also as it slightly dissolves in concentrated NaOH solution .

$$Bi_2O_3 + 6NaOH \longrightarrow \underset{\text{Sodium bismuthite}}{2Na_3BiO_3} + 3H_2O$$

The acidic nature of pentoxides decreases from N_2O_5 to Bi_2O_5 . N_2O_5 , P_2O_5 and As_2O_5 are soluble in water and form acids .

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \text{ (Nitric acid)}$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \text{ (Orthophosphoric acid)}$$

$$As_2O_5 + 3H_2O \longrightarrow 2H_3AsO_4 \text{ (Arsenic acid)}$$

Sb_2O_5 and Bi_2O_5 are insoluble in water but dissolve in alkalies

$$Sb_2O_5 + 6NaOH \longrightarrow \underset{\text{Sodium antimonate}}{2Na_3SbO_4} + 3H_2O$$

$$Bi_2O_5 + 6NaOH \longrightarrow \underset{\text{Sodium bismuthate}}{2Na_3BiO_4} + 3H_2O$$

Acidic nature of M_2O_4 oxides also decreases from N_2O_4 to Bi_2O_4 . The acidic nature of these oxides is less than X_2O_5 type and more than X_2O_3 type. The decrease in acidic nature of theoxides from nitrogen to bismuth is due to decrease in nonmetallic character and increase in metallic character from N to Bi .

(ii) In the oxides of a particular element , the acidic nature increases as the percentage of oxygen increases or as the oxidation state increases . For example , N_2O_5 is most acidic while N_2O_3 is less acidic , similarly P_2O_5 is more acidic than P_2O_3 and P_2O_4.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$
$$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$$
$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

HNO_3 is stronger than HNO_2.

$$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3$$
$$P_2O_4 + 3H_2O \longrightarrow H_3PO_4 + H_3PO_3$$
$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

H_3PO_4 is stronger than H_3PO_3.

(iii) Stability of oxides of higher oxidation states decreases with increasing atomic number.

Thermal stability decreases in each series from N to Bi. N_2O_3 is most stable oxide. It is more stable than other oxides.N_2O_5 is less stable. However, P_2O_5 is thermally stable, but As_2O_5 and Sb_2O_5 are less stable. Bi_2O_5 is least stable. Except P_2O_5. all the pentoxides show oxidising properties. N_2O_5 is the strongest oxidising agent.

Nitrogen forms two more oxides, nitrous oxide (N_2O) and nitric oxide (NO) . Both are neutral in nature. Structurally, the oxides of nitrogen are different from the oxides of the rest of the elements of this group . This is due to the fact that only nitrogen is able to form p_π- p_π multiple bonds which are present in its oxides . The rest of the elements do not form multiple bonds and prefer to form cage structures for their oxides .

(b) Oxyacids : All the elements of this group form oxyacids. Nitrogen forms a number of oxyacids but two common oxyacids are - nitrous acid (HNO_2) and nitric acid (HNO_3). Nitric acid is a stable acid while HNO_2 is unstable. Phosphorus forms a large number of oxyacids. The important oxyacids are:

H_3PO_2	H_3PO_3	$H_4P_2O_4$	H_3PO_4	HPO_3	$H_4P_2O_7$
Hypophosphorus acid	Phosphorus acid	Hypophosphorie acid	Orthophosphoric acid	Metaphosphoric acid	Pyrophosphoric acid

Arsenic forms two oxyacids, H_3AsO_3(arsenious acid) and H_3AsO_4 (arsenic acid). Antimony forms one oxyacid H_3SbO_3 which exists in solution Bismuth also forms on acid $HBiO_3$, meta - bismuthic acid.

The strength and stability of oxyacids having the element in the same oxidation state decreases gradually with decrease in electronegativity of central atom

HNO_3 H_3PO_4 H_3AsO_4 H_3SbO_4

Strong Weak Very weak Weakest

(c) Hydrides: All the elements of this group form hydrides of the type MH_3.

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Ammonia	Phosphine	Arsine	Stibine	Bismuthine

(ii) All the hydrides are formed by the action of water or dilute acids on binary metallic compounds such as Mg_3N_2 , Ca_3P_2 , Zn_3As_2 and Mg_3Bi_2.

The hydrides are also obtained by reduction of trichlorides of these elements (except that of bismuth) with Zn / acid or $LiAlH_4$.

$$4MCl_3 + 3LiAlH_4 \longrightarrow 4MH_3 + 3LiCl + 3AlC_3$$

$$(M = N , P , As , Sb)$$

(ii) All the hydrides are colourless gases. Their smell becomes more and more disagreeable as atomic number increases from N to Bi .

(iii) The poisonous nature increases from NH_3 to BiH_3 .

(iv) NH_3 is highly soluble in water but other hydrides are less soluble.

(v) The basic character decreases from NH_3 to BiH_3. The basic nature is due to the presence of lone pair of electrons on the central atom . NH_3 is the strongest electron pair donor due to its small size as the electron density of the electron pair is concentrated over a small region. As the size increases the electron density gets diffused over a large region and hence the ability to donate the electron pair (basic nature) decreases . NH_3 and PH_3 form NH_4^+ . and PH_4^+ ions with protons . NH_4^+ is more stable than PH_4^+ ion . PH_3 is less basic than NH_3 while AsH_3 , SbH_3 and BiH_3 are neutral . NH_3 is highly soluble in water while PH_3 is less soluble.

$$NH_3 + H_2O \longrightarrow \underset{\text{Weak base}}{NH_4OH} \quad : \quad PH_3 + H_2O \longrightarrow \underset{\text{Very weak base}}{PH_4OH}$$

(vi)Thermal stability decreases gradually from NH_3 to BiH_3.The decomposition temperatures decrease from NH_3 to BiH_3

NH_3	PH_3	AsH_3	SbH_3	BiH_3
1300°C	440°C	280°C	150°C	Room temp

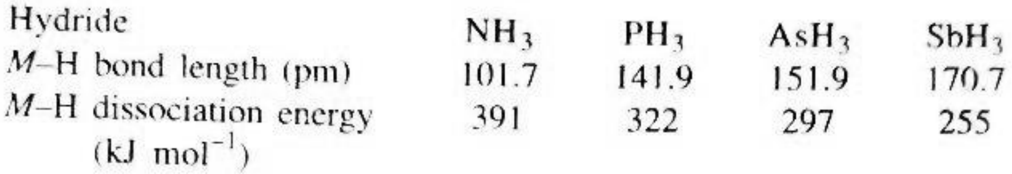
The size of the central atom increases from N to Bi , therefore , the tendency to form a stable covalent bond with small hydrogen atom decreases .As the bond length increases, the strength decreases and therefore , thermal stability decreases.

(vii) The reducing nature increases. This shows that bond strength *M*-H decreases as electronegativity of *M* decreases. NH_3 is a weak reducing agent while AsH_3,SbH_3 and $BiH_3$are powerful reducing agents.

(vii) The shape of these hydrides is pyramidal . The formation is due to sp^3 hybridization of central atom , i.e., forming a tetrahedral configuration. However, on one of tetrahedral positions, a lone pair of electrons is present. The bond angle (H *M* H) in various hydrides is never equal to ideal tetrahedral angle of 109°. 28'. The actual bond angles are:

NH_3	PH_3	AsH_3	SbH_3
107.5°	93.5°	91.5°	91.3°

The bond angle in ammonia is less than 109°.28' due to repulsion between lone pair present on nitrogen atom and bonded pairs of electrons . The decreased bond angle in other hydrides can be explained by the fact that the sp^3 hybridization becomes less and less distinct with increasing size of the central atom i.e., pure *p*-orbitals are utilised in *M*-H bonding. Bond lengths and bond dissociation energies of the hydrides of group 15 elements are listed below:



Hydride	NH_3	PH_3	AsH_3	SbH_3
M–H bond length (pm)	101.7	141.9	151.9	170.7
M–H dissociation energy (kJ mol^{-1})	391	322	297	255

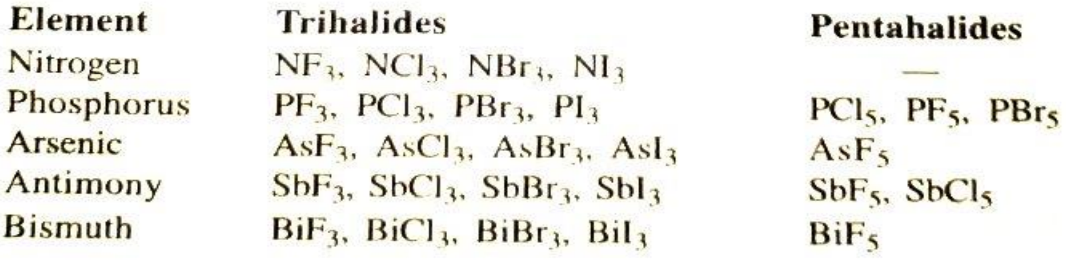
(ix)Hydrogen bonding: Hydrogen bonding is present in NH_3 as the electronegativity difference between nitrogen and hydrogen is high and the N-H bond shows polarity. The electronegativity of rest of the elements is nearly equal to hydrogen , hence *M*-H bond is purely covalent and no hydrogen bonding is present in their hydrides .

(x) The boiling points of these hydrides vary as follows:

Hydride	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Boiling point (°C)	-33	-89	-63	-9	17

In NH_3, molecules are associated by hydrogen bonding and thus its boiling is comparatively high in comparison to PH_3 and AsH_3 where no hydrogen bonding is present. In moving from PH_3 to BiH_3, boiling points increase due to increase in the magnitude of van der Waals ' forces due to increase in molecular size.

(d) Halides: The main halides formed by the elements of this group are listed below:



Element	Trihalides	Pentahalides
Nitrogen	NF_3, NCl_3, NBr_3, NI_3	—
Phosphorus	PF_3, PCl_3, PBr_3, PI_3	PCl_5, PF_5, PBr_5
Arsenic	AsF_3, $AsCl_3$, $AsBr_3$, AsI_3	AsF_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

All form trihalides. One or more pentahalides are formed by the elements except nitrogen. Nitrogen does not form pentahalides due to absence of *d*-orbitals.

(i) Trihalides: The elements directly combine with halogens and form trihalides , MX_3.All the trihalides are stable except NCl_3 , NBr_3 and NI_3.The unstable nature of NCl_3 NBr_3 and NI_3 is due to low polarity of N-X bond and a large difference in the size of nitrogen and halogen atoms.

The trihalides have a tetrahedral structure involving *sp^3* hybridization of the central atom. They have pyramidal shape. A lone pair of electrons is present on the central atom. Due to the presence of a lone pair of electrons on the central atom, they act as Lewis bases. In the case of nitrogen halides, the tendency to act as Lewis base decreases from $NI_3$to NF_3.

$$NI_3 > NBr_3 > NCl_3 > NF_3$$

This is due to increased electronegativity from I to F. Also the tendency to act as Lewis base decreases from N to Bi for a given halide.

The trihalides of phosphorus and antimony especially fluorides and chlorides act as Lewis acids also by using the vacant *d*-orbitals.

Except NF_3 and PF_3, all the trihalides are hydrolysed by water.

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HClO$$
$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$
$$AsCl_3 + 3H_2O \longrightarrow H_3AsO_3 + 3HCl$$
$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$$
$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

(ii)Pentahalides: Phosphorus pentachloride is the most well known of the pentahalides. Bismuth does not form pentahalides because of inert pair effect. The pentahalides have a trigonal bipyramid shape (*sp^3d* hybridization) in gaseous and liquid states which is not very stable structure, hence these pentahalides decompose into stable lower halides.

$$PCl_5 = PC_3 + Cl_2$$

These are also hydrolysed by water.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

[PCl_5 acts as an effective chlorinating agent.]

X-ray studies have shown that the solid PCl_5 is an ionic compound composed of $[PCl_4]^+$ $[PCl_6]^-$. Solid PBr_5 exists as $[PBr_4]^+Br^-$.

All the pentahalides act as Lewis acids due to the presence of *d*-orbitals.

$$MX_5 + X^- \longrightarrow [MX_6]^-$$

The hybridization of the central atom (*M*) changes from sp^3d to sp^3d^2.

(e) Sulphides: With the exception of nitrogen, all other elements of this group form sulphides. The sulphides of arsenic and antimony are soluble in yellow ammonium sulphide or ammonium sulphide and form thio-compounds.

$$As_2S_3 + 3(NH_4)_2S \longrightarrow \underset{\text{Ammonium thio-arsenite}}{2(NH_4)_3AsS_3}$$
$$As_2S_5 + 3(NH_4)_2S \longrightarrow \underset{\text{Ammonium thio-arsenate}}{2(NH_4)_3AsS_4}$$

Antimony sulphides form similar compounds. The sulphides are also soluble in caustic alkali.

$$As_2S_3 + 6NaOH \rightarrow \underset{\text{Sodium thioarsenite}}{Na_3AsS_3} + \underset{\text{Sodium arsenite}}{Na_3AsO_3} + 3H_2O$$

The stability of sulphides increases with increase in atomic number of the element.

ABNORMAL BEHAVIOUR OF NITROGEN

Nitrogen differs considerably from the rest of the family members. The differences or abnormal properties are mainly due to the following four factors:

(a) Small size of nitrogen atom.
(b) High value of electronegativity.
(c) Absence of *d*-orbitals in the valency shell.
(d) Tendency to form multiple bonds.

The important points in which nitrogen differs from other members of VA group are listed below:

(i) Nitrogen is a gas while other members are solids.

(ii) Nitrogen molecule is diatomic (N_2) while other elements form tetratomic molecules such as P_4, As_4 and Sb_4.

(iii)The catenation property is more pronounced in nitrogen. Chains containing upto eight nitrogen atoms are known but in the case of other elements, catenation is limited to two atoms only.

(iv)Nitrogen forms five oxides. N_2O (nitrous oxide), NO (nitric oxide), N_2O_3 (nitrogen trioxide), NO_2 (nitrogen dioxide) and N_2O_5 (nitrogen pentoxide). Others can form at the most three types of oxides, X_2O_3, X_2O_4 and X_2O_5.

N_2O_3 and N_2O_5 are monomeric in nature but oxides of other elements are dimeric.

(v) Hydride of nitrogen (NH_3) is stable while the hydrides of other elements are not stable. Hydrogen bonding is present in ammonia (NH_3) but not present in other hydrides.

(vi) Except NF_3, the halides of nitrogen (NCl_3, NBr_3 and NI_3) are unstable and explosive. The halides of other elements are stable. Unlike P, As and Sb, nitrogen does not form pentahalides.

(vii) Due to small size and high electronegativity, nitrogen can form trinegative ion N^{3-}. This tendency is less in P but absent in other elements.

(viii) As nitrogen does not have *d*-orbitals in its Valens shell, its maximum covalency is 3 while in the case of other elements, the maximum covalency is 5.

(ix)Nitrogen is chemically inert under ordinary atmosphere conditions. This is due to high dissociation energy of nitrogen molecule. The other elements are quite reactive as they have single bonds in their molecules, i.e., dissociation energies are low.

(x) Nitrogen shows a large number of oxidation states from -3 to +5 such as +1 in N_2O , +2 in NO , +3 in N_2O_3 , +4 in NO_2 , +5 in N_2O_5 , -1 in NH_2OH and -3 in NH_3. Other elements show a limited number of oxidation states from -3 to +5.

(xi)Nitrogen does not form sulphide while all other elements form sulphides.

(xii) On account of high value of electronegativity, nitrogen behaves as a typical non-metal while As, Sb are metalloids and Bi is a metal.

Nitrogen ($N \equiv N$), carbon monoxide $C \underset{\longleftarrow}{=} O$ and cyanide ion ($C \equiv N$) are isoelectronic in nature. Nitrogen is inert while other species are active. The bond between nitrogen atoms is non-polar.