

## P-BLOCK ELEMENTS

### VA GROUP ELEMENTS

#### SUBTOPIC-I

##### General characteristics, Hydrides, oxides and Halides

- Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth belong to VA group or 15 the group of the periodic table.
- Elements of Nitrogen family are called pnictogens and their compounds are called pnictides.
- The general valency shell electronic configuration of these elements is  $ns^2 ns^3$
- In air  $N_2$  occurs to the extent of 78% by mass or 80% by volume.
- In nature occurrence of VA group elements decreases from N to Bi
- From the structure of  $P_4$ . We can observe that each 'P' shares three of its valence electrons with other 'P' and one lone pair of  $e^-$  is seen on each 'P'
- Phosphorus atoms are larger in size hence lateral overlapping is not possible. So  $P_4$  molecules are formed by single bonds between p atoms.
- Nitrogen is chemically inert because  $N \equiv N$  energy is very high (945.4 K.J./ mole).
- There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and / or orbitals in heavier members.

##### Allotropic modifications:

- Except bismuth all the elements of this group exhibit allotropy.
- Nitrogen has two allotropes in the solid state.
- Phosphorus exists in a variety of forms. The most important forms of phosphorus are white or yellow, red,  $\alpha$ -Black,  $\beta$ -Black, scarlet, violet.
- In  $P_4$  molecule, the four P atoms are present at the corners of tetrahedron and bond angle is  $60^\circ$ .
- The allotropes of Antimony are yellow, metallic form and explosive forms.
- The catenation capacity depends on bond energy, Greater the bond energy value, higher the "catenation capacity".
- Catenation capacity decreases from N- Bi

##### Oxidation states:

- VA group's elements exhibit -3, +3 and +5 oxidation number.

- Stable oxidation number of Bi is +3 due to inert pair effect.

### Hydrides:

- The ability to donate lone pair (Lewis basic nature), stability, solubility and basic strength of the hydrides decrease from  $\text{NH}_3$  to  $\text{BiH}_3$
- $\text{NH}_3$  is best ligand and forms coordinate covalent bonds readily.
- $\text{MH}_3$  type hydrides are trigonal pyramidal in shape.
- In  $\text{MH}_3$  type hydrides, the bond angle decreases from  $\text{NH}_3$  to  $\text{BiH}_3$  due to increase in the size of atom M and decrease in the E.N.
- $\text{PH}_3$  is quite stable in air. But,  $\text{PH}_3$  frequently contains  $\text{P}_2\text{H}_6$  (diphosphine) in traces as impurity so when heated to  $150^\circ\text{C}$   $\text{P}_2\text{H}_6$  catches fire.
- (3) The lone pair of  $e^-$  is spread over a larger atom. As a result of this  $e^-$  donating nature (basic nature) decreases Stability order of hydrides  
 $\text{NH}_3 \gg \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 \gg \text{BiH}_3$
- Order of basic nature  
 $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
- Melting point  $\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$   
Boiling point  $\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3$   
Bond length  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$   
Bond energy  $\text{NH}_3 > \text{PH}_3 > \text{SbH}_3 > \text{AsH}_3$   
Bond angle  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$
- As pure 'p' orbitals of As and Sb are involved, the H-M-H bond angle in  $\text{AsH}_3$  would be expected  $90^\circ$ . But due to repulsions between M-H bonds, the angle increases to  $91^\circ.48'$ .

### Oxides:

- These elements form two series of oxides – Trioxides ( $\text{M}_2\text{O}_3$ ) and Pentoxides ( $\text{M}_2\text{O}_5$ ).  
Nitrogen forms number of oxides due to  $P\pi - P\pi$  multiple bonding between N and oxygen atoms.  
As oxidation number of the element increases, acidic nature of its oxides increases

- Acidic nature of pentoxides is more than that of trioxides.
- Trioxides and pentoxides of P, As and Sb are dimers.
- The most acidic trioxide is  $N_2O_3$  and most basic trioxide is  $Bi_2O_3$  the acidic and basic nature of an oxide depends on the size and charge on the V<sup>th</sup> group element.

- $N_2O$ : Nitrous oxide (or) Nitrogen monoxide.

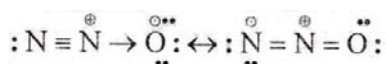
It is also known as laughing gas.

It is prepared by heating ammonium nitrate.

It is a colourless neutral oxide

It is a linear molecule.

- The structure of  $N_2O$  is



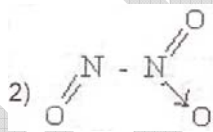
Usually  $N_2O$  is administered to the patient to put him to sleep

- **NO**: Nitric oxide; It is formed as an intermediate in the manufacture of  $HNO_3$  by catalytic oxidation of  $NH_3$  in presence of Pt.

- Its structure is  $:\overset{\cdot\cdot}{N} = \overset{\cdot\cdot}{O}:$

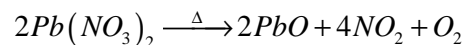
- $N_2O_3$ : Nitrogen trioxide :

- The following two structures are proposed.



- **NO<sub>2</sub>** (or) **N<sub>2</sub>O<sub>4</sub>**: Nitrogen dioxide or Dinitrogen tetroxide

It is obtained by heating Lead Nitrate.



- It is a reddish brown poisonous gas soluble in water.

It becomes a colourless solid on cooling due to the formation of dimer  $N_2O_4$ .

It dissolves in water giving  $HNO_2$  and  $HNO_3$ . So it is called mixed anhydride.

➤  $\text{NO}_2$  is an odd electron molecule and exhibits paramagnetic property.

In dimeric state ( $\text{N}_2\text{O}_4$ ) it is colourless and diamagnetic in nature

➤  $\text{N}_2\text{O}_5$ : Dinitrogen pentoxide.

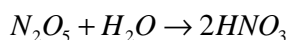
It is obtained by dehydrating  $\text{HNO}_3$  with  $\text{P}_2\text{O}_5$ .

It is the anhydride of Nitric acid.

It is a powerful oxidizing agent.

It is a colourless solid.

It dissolves in water to give nitric acid.



It has planar structure and is represented as

### Oxides of Phosphorus:

➤  $\text{P}_4\text{O}_6$  : Phosphorus trioxide

It is obtained by burning phosphorus in limited supply of air.

It is the anhydride of phosphorus acid.

It dissolves in cold water to form phosphorus acid.

In  $\text{P}_4\text{O}_6$  each phosphorus is surrounded by three oxygen atoms.

It is an acidic oxide.

Numbers of P-O-P bonds are six

➤  $\text{P}_4\text{O}_{10}$  : Phosphorus trioxide

It is obtained by burning phosphorus in excess of air or oxygen.

It is the anhydride of phosphoric acid.

It dissolves in water to form  $\text{H}_3\text{PO}_4$ .

In  $\text{P}_4\text{O}_{10}$  each phosphorus is surrounded by four oxygen atoms.

Numbers of P-O-P bonds are six

It is a strong dehydrating agent

From  $N_2O_3$  to  $Bi_2O_3$  acidic nature decreases and basic nature increases.

Acidic nature decreases or basic nature increases from  $N_2O_5$  to  $Sb_4O_{10}$

**Halides:**

- ❖ VA group elements form trihalides of the type  $MX_3$  and pentahalides of the type  $MX_5$ .

Trihalides are prepared by the reaction of VA group element or its compound with halogen.  $NF_6$  does not undergo hydrolysis.

$NCl_3$  on hydrolysis gives  $NH_3$  and Hypochlorous acid.

$PF_3$  is weakly reactive to water

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

$PCl_3$  on hydrolysis gives  $HCl$  and  $H_3PO_3$

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

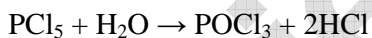
Tri halides are covalent.

Trihalides use the  $sp^3$  hybridised orbitals of the central atom.

- Nitrogen cannot form  $NCl_5$  because it has no d-orbitals in the valency shell.

$PCl_5$  is obtained by passing  $Cl_2$  into liquid  $PCl_3$ .

$PCl_5$  undergoes a two step hydrolysis.



- Bi does not form  $BiCl_5$  due to inert pair effect.

Penta halides use the  $sp^3d$  hybridized orbitals of the central atom.

- Pentahalides have trigonal bipyramidal structure.

The extent of hydrolysis decreases from  $NX_3$  to  $BiX_3$ .

- The tendency to act as Lewis base decreases from  $NI_3$  to  $NF_3$  (Due to increased E.N from I to F)
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## VA GROUP ELEMENTS (SUBTOPIC-II)

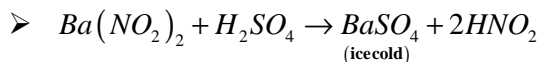
**Oxyacides of Nitrogen, Phosphorous, ammonia and super phosphate of lime:**

**Oxyacides of Nitrogen:**

➤ **Nitrous acid (HNO<sub>2</sub>):**

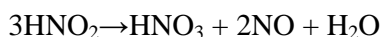
Nitrous acid is unstable except in dilute solutions

In the laboratory it is prepared by the addition of ice cold dilute acid to Barium nitrite



Its solution is slightly bluish in colour due to the presence N<sub>2</sub>O<sub>3</sub>.

➤ On standing it undergoes auto oxidation-reduction in acidic solution



In this reaction

In HNO<sub>2</sub> → HNO<sub>3</sub> O.S of 'N' changes from +3 to +5

In HNO<sub>2</sub> → NO O.S of N changes from +3 to +2 i.e. "HNO<sub>2</sub>"

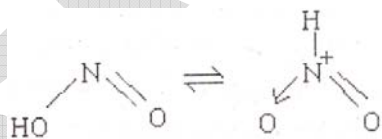
➤ With oxidizing agents stronger than HNO<sub>2</sub> like

KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, Br<sub>2</sub> + H<sub>2</sub>O or H<sub>2</sub>O<sub>2</sub> solutions HNO<sub>2</sub> functions as reductant.

Where as with weaker oxidants i.e. reducing agents like H<sub>2</sub>S, SO<sub>2</sub> 'or' Sn<sup>+2</sup> solutions HNO<sub>2</sub> functions as oxidant

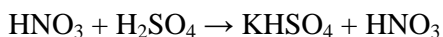
➤ Structure of (HNO<sub>2</sub>):

HNO<sub>2</sub> exists in two tautomeric forms i.e. in two structural isomers.

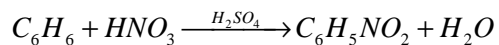


➤ **Nitric acid (HNO<sub>3</sub>) : "Aqua fortis"**

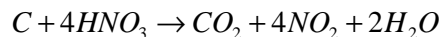
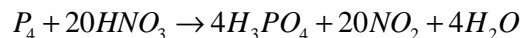
➤ In laboratory it is prepared by the action of conc. H<sub>2</sub>SO<sub>4</sub> on KNO<sub>3</sub> or NH<sub>4</sub> NO<sub>3</sub>



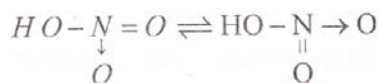
- A mixture of 1 : 1 conc.  $\text{HNO}_3$  and Conc.  $\text{H}_2\text{SO}_4$  is known as nitration mixture  
It is used in nitration reaction of organic compounds like Benzene, Toluene and phenol



- It is a very strong oxidizing agent. It oxidises non-metals to their corresponding oxides or oxoacids



- The structure of nitric acid is



This is a monobasic acid

It is a strong oxidizing agent

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

- i) It oxidises iodine to iodic acid



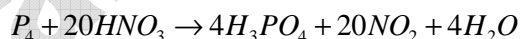
- ii) Carbon to carbon dioxide,



- iii) Sulphur to  $\text{H}_2\text{SO}_4$



- iv) Phosphorus to phosphoric acid



- **Oxyacids of phosphorus:**

The phosphorous series of acids contains P-Hbonds

P-H bonds are responsible for reducing property of our acids

O-H bonds are responsible for acidic properties.

➤ **Hypo Phosphorous acid ( $H_3PO_2$ ):**

It is prepared by the heating yellow or white 'p' with dilute  $Ba(OH)_2$

$6H_2O + 2P_4 + 3Ba(OH)_2 \rightarrow 3Ba(H_2PO_2)_2 + 2PH_3\uparrow$  from  $Ba(H_2PO_2)_2$ ,  $H_3PO_2$  is obtained by hydrolysis.

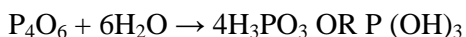
➤  $H_3PO_2$  is monobasic acid and a very strong reducing agent in basic solutions and it is oxidized to  $H_3PO_3$

➤ **Meta phosphorous acid ( $HPO_2$ )**

It is mono basic acid normally exist as a cyclic compound due to polymerization.

➤ **Ortho phosphorous acid ( $H_3PO_3$ )**

It is prepared by dissolving  $P_4O_6$  in cold  $H_2O$



It forms two types of salts

1) primary phosphates  $H_2PO_3^-$  (dihydrogen phosphate)

2) secondary phosphates  $HPO_3^{-2}$  (monohydrogen phosphates)

➤ **Ortho Phosphoric acid ( $H_3PO_4$ ):**

➤ It is prepared by dissolving  $P_4O_{10}$  in water



➤ It is a weak tribasic acid has oxidizing properties.

➤ Solid  $H_3PO_4$  absorbs water and forms a colourless syrupy liquid (syrupy phosphoric acid)

➤ In qualitative analysis orthophosphates are identified by ammonium phospho molybdate formation (Molybdate test)

➤ **Meta Phosphoric acid ( $HPO_3$ ):**

➤ Phosphoric acid. It is formed by heating pyrophosphoric acid or orthophosphoric acid to 870 K

➤ It is transparent glassy solid.

$HPO_3$  is a monobasic acid and its salts are called meta phosphates.

There is no evidence for the existence of true monophosphate ( $PO_3^-$ ) ions or of the dimeta phosphate ( $P_2O_6^{-2}$ ) or ( $PO_3^-$ )<sub>2</sub>. but tri and tetra meta phosphates are well known. They form a family of ring compounds.



- Calcium super phosphate is manufactured by the action of conc.  $H_2SO_4$  (chamber) acid and powdered bone ash or calcium phosphate.
- The impurities in phosphate rock i.e. carbonates liberated as  $CO_2$  and fluoride liberated as HF gases.
- Calcium super phosphate is  $Ca(H_2PO_4)_2 + 2(CaSO_4 \cdot 2H_2O)$
- The  $CaSO_4$  in super phosphate of lime is an insoluble waste product.  
To avoid this waste product, the super phosphate is converted into “Triple phosphate” by treating with “ $H_3PO_4$ ”

