

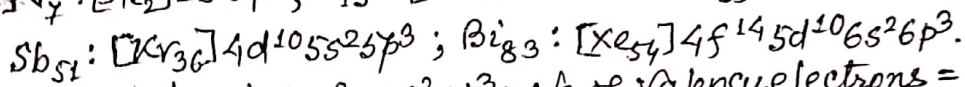
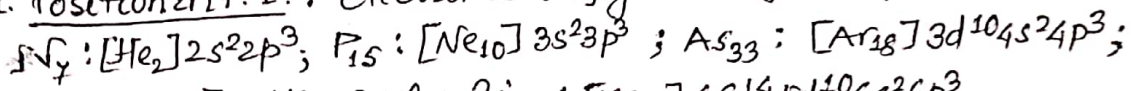
B.Sc-III Hons, Paper-6 (Inorganic Chem), Group-B

Unit-1 General Chemistry of Group-15 (Nitrogen group) elements

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Group-15 of modern periodic table consists of six elements: Nitrogen ( $N_7$ ), Phosphorus ( $P_{15}$ ), Arsenic ( $As_{33}$ ), Antimony ( $Sb_{51}$ ), Bismuth ( $Bi_{83}$ ) & Moscovium ( $Mc_{115}$ ). They are called 'Nitrogen family', and also 'Pnicogens' (Greek Pnicomings, meaning suffocating). The general chemistry of Group-15 elements are as follows:

⇒ 1. Position in P.T.: Electronic configuration of Group-15 elements are:



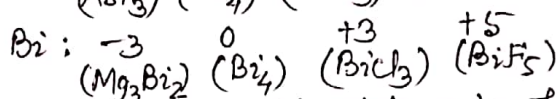
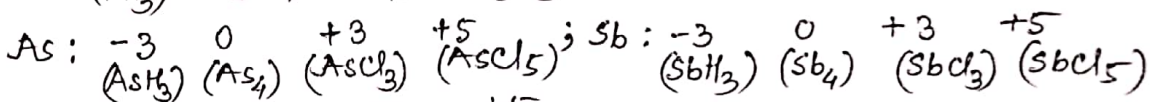
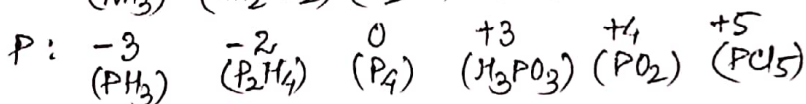
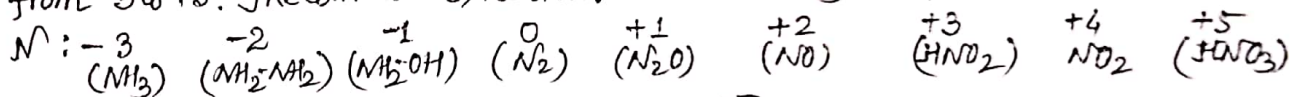
Outer electronic Conf.  $ns^2 np^3$ ; No. of valency electrons = 5

Block-P (Since last electron occupy in p-subshell or orbital), Group = 10 + 5 = 15

Periods: 2 (for N), 3 (for P), 4 (for As), 5 (for Sb), 6 (for Bi)

Thus, they are placed in Group-15 between Gr.14 (Carbon group) & Gr.16 (Oxygen group) under p-block in the modern Periodic table. They resemble in their properties and hence occupy same position (Gr.15).

⇒ 2. Oxidation states: The valence or outermost orbit of N-group (Gr.15) has 5 electrons ( $ns^2 np^3$ ). They can attain stable configuration either by donating 5 electrons or gaining 3 electrons or five orbitals for hybridisation (s, 3p & d) which form maximum five covalent bonds/covalency. Oxidation states may range from -3 to +5. The common Oxidation states shown by Group-15 elements are:



\* N & P show Oxidation state -3, i.e. forming ( $N^{3-}$ ) nitrides, phosphide ( $P^{3-}$ ) with highly electro positive metals. Rest (As, Sb, Bi) show Oxidation state -3 forming covalent compounds

\* Oxidation state -2 is shown by N & P in hydrazine ( $NH_2NH_2$ ) & diphosphine ( $PH_2PH_2$ ) res.

\* Oxidation state -1 is shown only by N; in  $NH_2OH$  (hydroxylamine).

\* N & P show Oxidation states +1, +2 & +4.

\* Oxidation states +3, +4 & +5 are most common and shown by all elements of Gr.15.

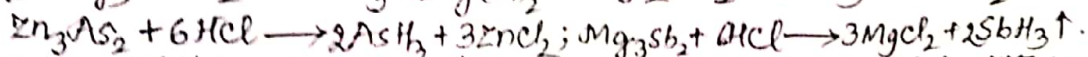
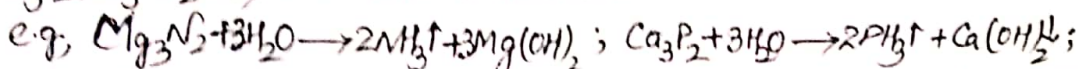
\* The O. state +3 is covalent & ionic (e.g.  $Bi_2F_3$ ,  $SbF_3$ ), while O. state +5 is covalent.

The covalent character decrease from N to Bi, i.e.  $N > P > As > Sb > Bi$ .

\* On moving down the group, tendency to show O. state +3 increases & O. state +5 become less stable. Highest O. state +5 is common with highly electronegative elements (F, O, N etc.)

⇒ 3. Formation of hydrides: All the elements of Group 15 form hydrides of types  $MH_3$  &  $M_2H_4$  (in case of N & P only).  $MH_3$  type hydrides:  $NH_3$  (Ammonia),  $PH_3$  (Phosphine),  $AsH_3$  (Arsine),  $SbH_3$  (stibine),  $BiH_3$  (Bismuthine);  $M_2H_4$  type hydrides:  $N_2H_4$  (Hydrazine),  $P_2H_4$  (Diphosphine).

\*  $MH_3$  type hydrides are prepared by action of binary metal compounds (e.g;  $Mg_3N_2$ ,  $Ca_3P_2$ ,  $Zn_3As_2$  etc.) with water or dilute mineral acids.



Hydrazine ( $N_2H_4$ ) can be prepared by the action of  $NH_3$  (ammonia) with sodium hypochlorite ( $NaOCl$ ).  $2NH_3 + NaOCl \rightarrow NaCl + N_2H_4 \uparrow + H_2O$ .

\* Thermal stability: Hydrides of Gr. 15 are thermally stable and stability of hydrides decreases from  $NH_3$  to  $BiH_3$ . This is due to decrease of bond ( $M-H$ ) energy with the increase of size of element (i.e; atomic radius). The order of stability of hydrides:  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$  (Radii order:  $N < P < As < Sb < Bi$ ).

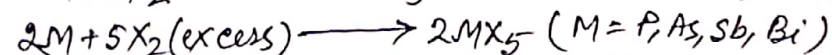
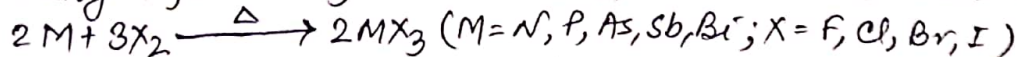
\* Basic character: They are basic in nature due to presence of lone pair of electron on central atom (M). The basic character of hydrides decrease from  $NH_3$  to  $BiH_3$ , i.e. order of basic character:  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ . As the electronegativity of central atoms decreases from N to Bi, lone pair causes greater distortion, suggesting that the lone pair occupies a spherical s-orbital, so donation of lone pair (i.e; the donor property) decreases from N to Bi.

\* Reducing property: Reducing property of the hydrides are high, i.e; they are strong reducing agents. Their reducing property increase from  $NH_3$  to  $BiH_3$  as bond energy of  $M-H$  bond decrease from  $NH_3$  to  $BiH_3$ . Lesser the bond energy more the reducing property.

\* Bond angle: Central atoms of hydrides of Gr. 15 are  $sp^3$  hybridized. One of the hybrid orbital has lone pair of electrons. Actual bond angle for  $sp^3$  hybrid molecule/tetrahedral is  $109^\circ 28'$ . Since the repulsion between a lone pair & a bond pair (l.p.-b.p) electrons always more than b.p.-b.p electrons, the regular tetrahedral shape/angle distorted (pyramidal, bond angle  $< 109^\circ 28'$ ). Further, as the electronegativity of the central elements/atoms decreases, the bond pairs become further away from the central atom, hence the l.p. causes greater distortion, so bond angle decreases from  $NH_3$  to  $BiH_3$ .

Order of hydrides w.r.to bond angle:  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$   
 (106.5°) (94°) (91.5°) (91.2°) (90°) of  $M-H$  bonds  
 \* Covalent nature: Hydrides of Gr. 15 are Covalent nature (polar). Polarity/Covalent nature of hydrides decreases from  $NH_3$  to  $BiH_3$  as electronegativity decrease from N to Bi (3.0 to 1.8).

⇒ 4. Formation of halides: All elements of Group-15 (except N) form two series of halides directly with halogen ( $X_2$ ):  $MX_3$  (trihalides) &  $MX_5$  (pentahalides). Nitrogen forms only trihalides ( $NX_3$ ) & does not  $NX_5$  due to absence of d-orbital.



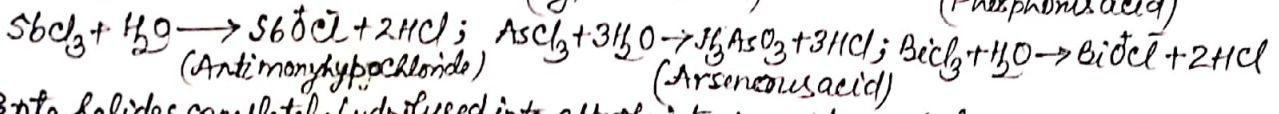
\* All the trihalides ( $MX_3$ ), except  $NX_3$  are stable. They are covalent nature. ( $BiF_3$  is ionic) and have a distorted tetrahedral structure ( $sp^3$  hybridized).

Covalent character of  $MX_3$  (trihalides) decreases from  $NX_3$  to  $BiX_3$  since difference of electronegatives of M & X increase. For a particular element (M), order of covalent character of different trihalides is as follows:  $MF_3 < MCl_3 < MBr_3 < MI_3$  since electronegativity order is  $F > Cl > Br > I$ . decrease

\* Basic character: Trihalides of Gr. 15 elements are basic character. Their basic character <sup>decrease</sup> from  $MI_3$  to  $MF_3$  (for same element), and increase from  $NX_3$  to  $BiX_3$  (for same halogen). Since electron donor tendency decrease with the increase of electronegativity. They act as Lewis bases.

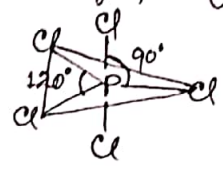
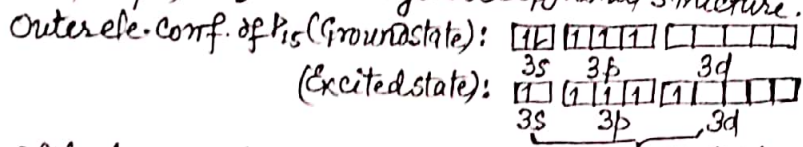
\* Stability: Trihalides of Gr. 15 elements are fairly stable (exceptions:  $NCl_3, NBr_3$  &  $NI_3$ ).  $NF_3$  is stable, but  $NCl_3$  is explosive, and  $NBr_3, NI_3$  are known only as unstable ammoniates.  $NX_3 \cdot 6MH_3$  (X = Cl, Br, I). The order of stability of trihalides:  $BiX_3 > SbX_3 > AsX_3 > PX_3 > NX_3$ ;  $NF_3 > NCl_3 > NBr_3 > NI_3$ .

\* Hydrolysis: All trihalides (except  $NF_3, PF_3$ ) are hydrolysed by water to form different compounds. e.g.,  $NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$  (Hypochlorous acid);  $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$  (Phosphorous acid)



Penta halides completely hydrolysed into appropriate-ric acid. e.g.,  $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$  (Orthophosphoric acid)

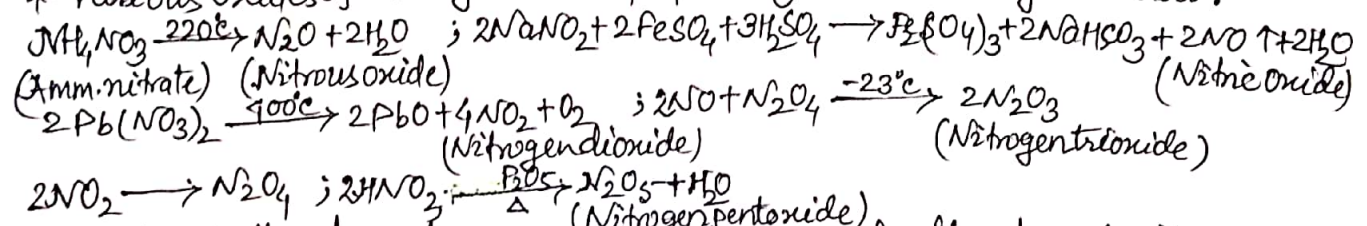
\* Pentahalides ( $MX_5$ ) molecules have a trigonal bipyramid shape in the gas phase, due to expansion of valency by shift of <sup>one</sup> ns electron to one of <sup>one</sup> nd orbital giving  $sp^3d$  hybridisation. For example,  $PCl_5$  has a trigonal bipyramid structure.



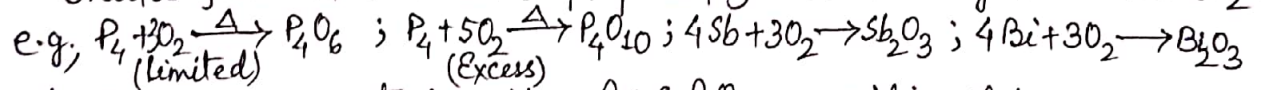
$NCl_5$  does not form since it has no d-orbital in which ns electron can be shifted and expand its valency 5 from  $3(2s^2 2p^1)$ .

5. Formation of Oxides & Oxyacids: Group-15 elements mainly form oxides of type  $M_2O_3, M_2O_4$  &  $M_2O_5$ . Besides these three types of oxides, nitrogen (N) also forms three more oxides viz.  $N_2O$  (Nitrous oxide),  $NO$  (Nitric oxide) &  $NO_2$  or  $N_2O_4$ . Bismuth also forms  $BiO$ . Oxides of nitrogen are monomeric, except  $NO_2$  which exists as  $N_2O_4$ , while many oxides of other elements are dimeric e.g.,  $(P_2O_3)_2$  or  $P_4O_6, (P_2O_5)_2$  or  $P_4O_{10}, As_4O_6, Sb_4O_6$  etc.

\* Various Oxides of nitrogen can be prepared by the reactions given below:



Oxides of other elements can be prepared by direct heating element with  $O_2$ .



\*  $N_2O$  &  $NO$  are neutral oxides.  $N_2O_3$  &  $P_2O_3$  are acidic while  $As_2O_3, Sb_2O_3$  &  $Bi_2O_3$  are amphoteric. All the pentoxides are acidic and their acidic character decrease quite sharply from  $N_2O_5$  to  $Bi_2O_5$ . The acidic nature of Oxides of a given element in different oxidation states increases with the increase of O. state, e.g.  $N_2O_5^{+5} > N_2O_4^{+4} > N_2O_3^{+3}$ . Pentoxides of these elements are strong oxidising agents.

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The pentoxides of Gr. 15 elements are thermally unstable.

Trioxides of these elements ( $M_2O_3$ ) are oxidised into higher oxides ( $M_2O_5$ ). Their thermal stability increase down the group, i.e.,  $N_2O_3 < P_2O_3 < As_2O_3 < Sb_2O_3 < Bi_2O_3$ .

All the elements of Gr. 15 form oxyacids. The important oxyacids of it are:

- (i) Hyponitrous acid ( $H_2N_2O_2$ ) (ii) Nitroxyl acid ( $H_2N_2O_3$ ) (iii) Nitrous acid ( $HNO_2$ )
- (iv) Nitric acid ( $HNO_3$ ) (v) Peroxonitric acid ( $HNO_4$ ).  $HNO_3$  is stable, strong monobasic acid and strong oxidising agent.

Important oxyacids of P are: (i) Hypophosphorous acid ( $H_3PO_2$ ) (ii) Phosphorous acid ( $H_3PO_3$ ) (iii) Orthophosphoric acid ( $H_3PO_4$ ) (iv) Metaphosphoric acid ( $H_4P_2O_7$ ) (v) Hypophosphoric acid ( $H_4P_2O_6$ ) (vi) Pyrophosphoric acid ( $H_4P_2O_7$ ).  $H_3PO_4$  is stable, strong tribasic acid and strong oxidising agent.

Arsenic forms two oxyacids:  $H_3AsO_3$  (Arsenious acid) &  $H_3AsO_4$  (Arsenic acid)

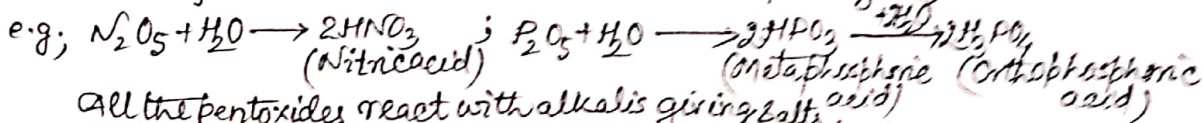
Antimony forms one oxyacid,  $H_3SbO_3$  (Antimonous acid) which exists in solution.

Bismuth also form one stable oxyacid,  $HBiO_3$  (Metabismuthic acid)

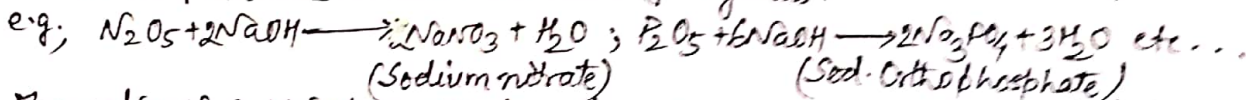
The strength and stability of oxyacids having the element in the same oxidation state decrease down the group, i.e.,  $HNO_3 > H_3PO_4 > H_3AsO_4 > H_3SbO_4 > HBiO_3$ .

The strength & stability of oxyacids of an element increases with the increase in its oxidation states, e.g.,  $HNO_3 > HNO_2$ .

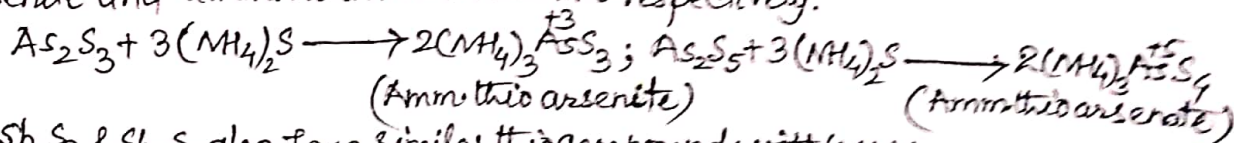
Oxides of N & P dissolve in water to form corresponding oxyacids.



All the pentoxides react with alkalis giving salts.

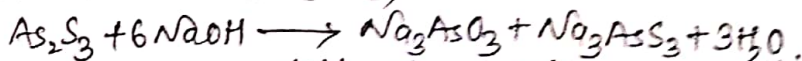


6. Formation of Sulphides: All elements of Gr. 15 (except N) form sulphides of types  $M_2S_3$  &  $M_2S_5$  ( $M = P, As, Sb \& Bi$ ).  $As_2S_3$  &  $As_2S_5$  are soluble in yellow ammonium sulphide or ammonium sulphide,  $(NH_4)_2S$ , and form ammonium thioarsenite and ammonium thioarsenate respectively.

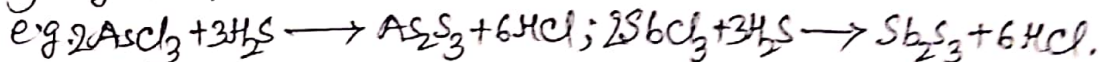


$Sb_2S_3$  &  $Sb_2S_5$  also form similar thio compounds with  $(NH_4)_2S$ .

$As_2S_3$  is soluble in  $NaOH$  and forms a mixture of sodium arsenite ( $Na_3AsO_3$ ) and sodium thioarsenite ( $Na_3AsS_3$ ).



Sulphides of N are very unstable. The stability of sulphides increases from N to Bi. The three elements of Gr. 15 (i.e., As, Sb & Bi) are all precipitated by hydrogen sulphide ( $H_2S$ ) gas from their salts solution in acidic medium (HCl).



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