

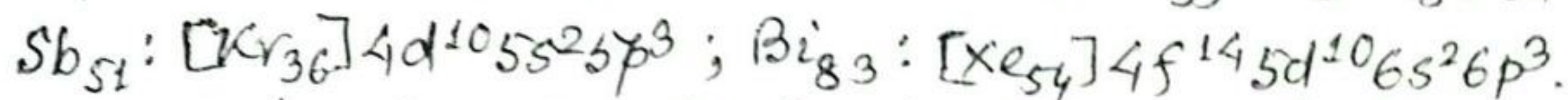
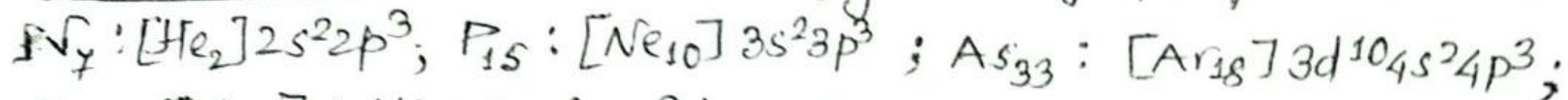
B.Sc-III Hone, Paper-6 (Inorganic Chem), Group B

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

(By Dr. Birendra Kumar, Maharaja College)

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:



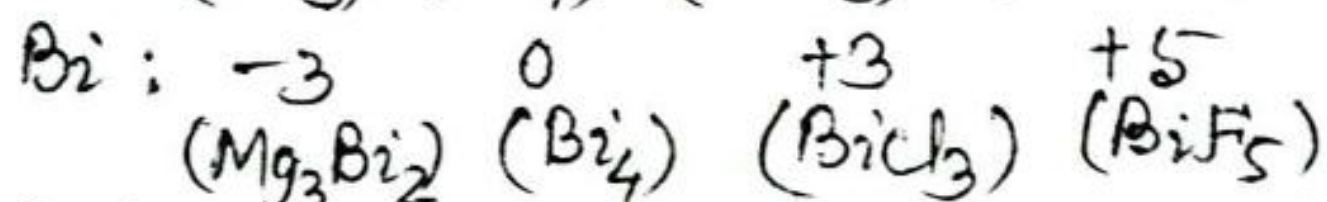
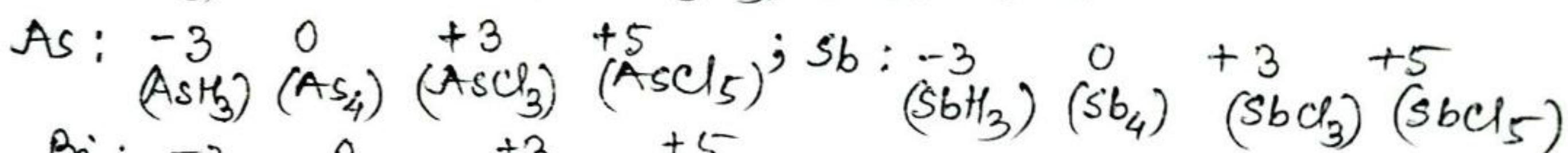
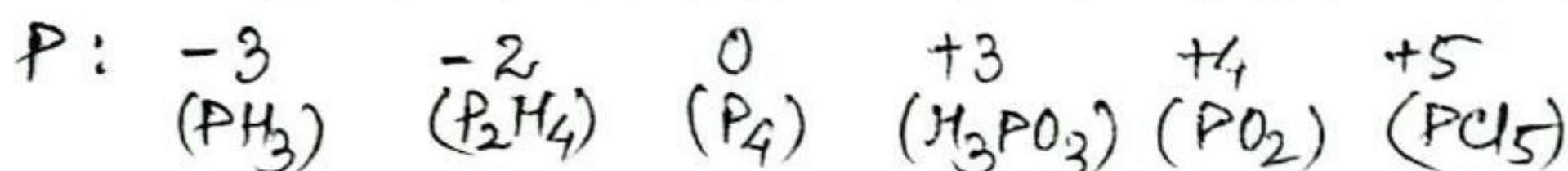
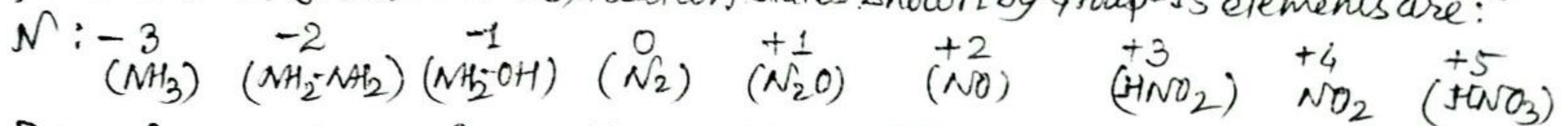
Outer electronic Conf. $ns^2 np^3$; No. of valency electrons = 5

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) resp.

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

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

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

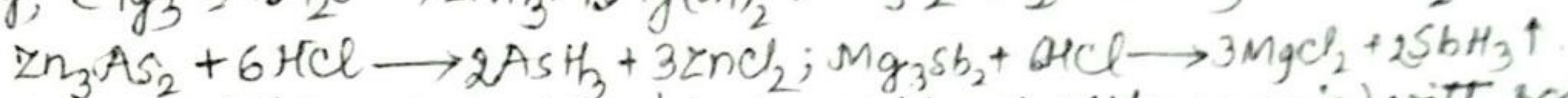
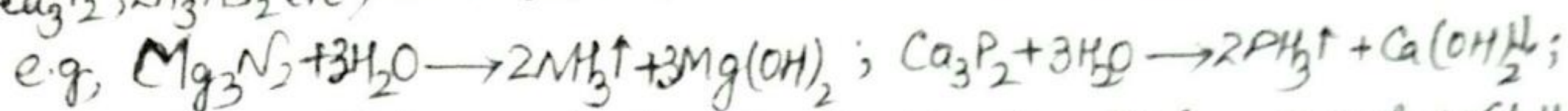
* The O. state +3 is ^{both} covalent & ionic (e.g. NCl_3 , PCl_3), while O. state +5 is covalent.

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: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ (radius order: $N < P < As < Sb < Bi$).

* Basic character: They are basic in nature due to presence of lone pair of electrons 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.

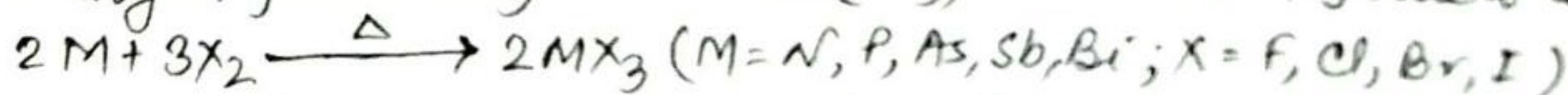
* Bond angle: Central atoms of hydrides of Gr. 15 are sp^3 hybridized. One of the hybrid orbital has lone pair of electrons. Actual bond angle for sp^3 hybrid molecule/tetra-hedral is $109^\circ 28'$. Since the repulsion between a lone pair & a bond pair (l.p.-b.p) electrons always more than b.p.-b.p 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: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

* 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 (tri halides) & MX_5 (Penta halides).

Nitrogen forms only trihalides (NX_3) & does not NX_5 due to absence of d-orbital.



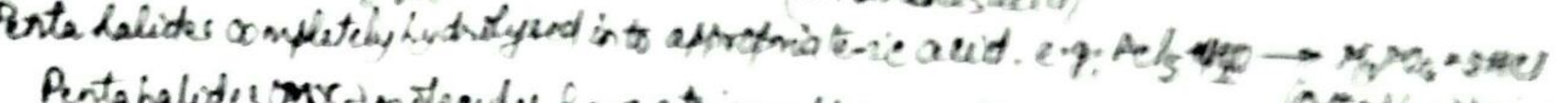
* All the trihalides (MX_3), except NX_3 are stable. They are covalent nature (BiF_3 is ionic) and have a distorted tetrahedral structure (sp^3 hybridized.)

Covalent character of MX_3 (the halides) increases from NX_3 to BiX_3 , since difference of electronegativities 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 $F > Cl > Br > I$.

* Basic character: Trihalides of Gr. 15 elements are basic in character. Their basic character increases from MCl_3 to MF_3 (for same element), and increase from NX_3 to BiX_3 (for same halogen). Since electron donor tendency decreases with the increase of electronegativity. They act as Lewis bases.

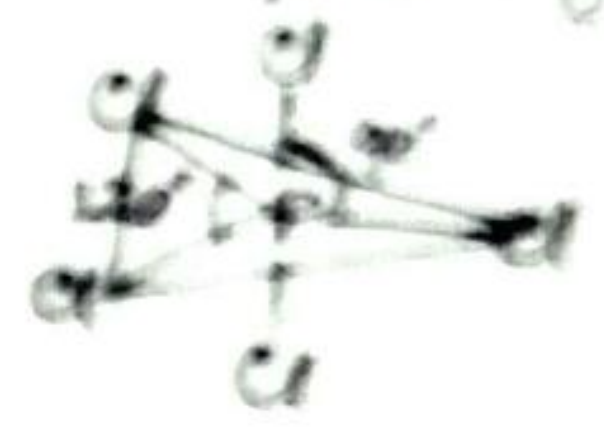
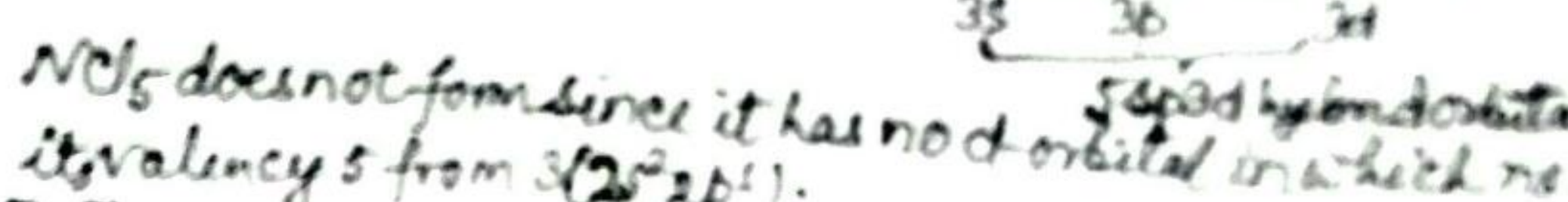
* Stability: Trihalides of Gr. 15 elements are fairly stable (exceptions: NCl_3, NBr_3, NI_3). NCl_3 is stable but NCl_3 is explosive, and NBr_3, NI_3 are known only as unstable ammoniates $NCl_3 \cdot 6NH_3$ (and $NBr_3 \cdot 6NH_3$). The order of stability of trihalides: $BiX_3 > SbX_3 > AsX_3 > PCl_3 > NX_3$; $NF_3 > NCl_3 > NBr_3 > NI_3$.

* Hydrolysis: All trihalides (except NF_3, PF_3) are hydrolyzed 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 hydrolyzed into appropriate acid. e.g., $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ (Orthophosphoric acid).

* Pentahalides (MX_5) molecules have a trigonal bipyramidal shape in the gas phase, due to expansion of valency by shift of n s electrons to one of n d orbital giving sp^3d hybrid orbitals. For example, PCl_5 has a trigonal bipyramidal structure.



NO_5 does not form since it has no d-orbital in which n s electrons can be shifted and expand its valency 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) & N_2O_4 or N_2O_2 . Bi with 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., $(P_2O_3)_2 \sim P_4O_6, (P_2O_5)_2 \sim P_4O_{10}, As_2O_3, Sb_2O_3$ etc.

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

$NH_4NO_3 \xrightarrow{220^\circ C} N_2O + 2H_2O$; $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2NO + 2H_2O$
 (Ammonium nitrate) (Nitrous oxide) (Nitric oxide)

$2Pb(NO_3)_2 \xrightarrow{900^\circ C} 2PbO + 4NO_2 + O_2$; $2NO + N_2O_4 \xrightarrow{-23^\circ C} 2N_2O_3$
 (Nitrogen dioxide) (Nitrogen trioxide)

$2NO_2 \rightarrow N_2O_4$; $2MNO_2 \xrightarrow{P_2O_5} M_2O_5 + H_2O$ (Nitrogen pentoxide)

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

e.g., $P_4 + 3O_2 \xrightarrow{\Delta} P_4O_6$ (limited) ; $P_4 + 5O_2 \xrightarrow{\Delta} P_4O_{10}$ (Excess) ; $4Sb + 3O_2 \rightarrow Sb_2O_3$; $4Bi + 3O_2 \rightarrow Bi_2O_3$

* 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., $N_2O_5 > N_2O_4 > N_2O_3$. Pentoxides of these elements are strong oxidising agents.

1. The pentoxides of Gr. 15 elements are normally unstable.

Trioxides of these elements (M_2O_3) are oxidised into higher oxides (M_2O_5) 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 N are:
 (i) Hyponitrous acid ($H_2N_2O_2$) (ii) Nitrous acid (HNO_2) (iii) Nitric acid (HNO_3) (iv) Nitric acid (HNO_3) (v) Peroxonitric acid (HNO_4). HNO_3 is stable, strong 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 (HPO_3) or Pyrophosphoric acid ($H_4P_2O_6$) (v) Pyrophosphoric acid ($H_4P_2O_7$). H_3PO_4 is stable, tribasic acid and strong oxidising agent.

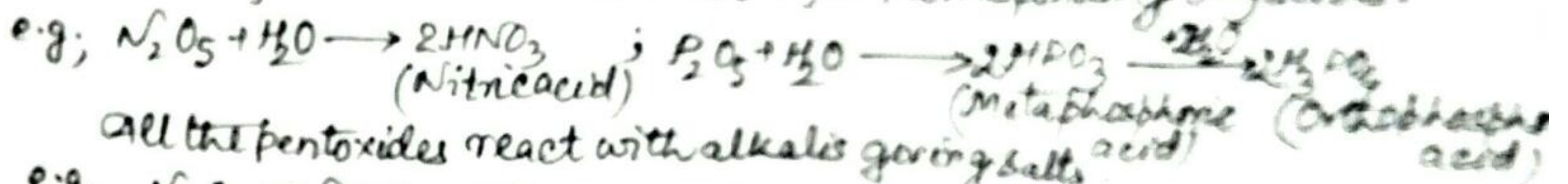
Arsenic forms two oxyacids: H_3AsO_3 (Arsenious acid) & H_3AsO_4 (Arsenic acid).
 Antimony forms one oxyacid, H_3SbO_3 (Antimonous acid) which exists.

Bismuth also forms 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., $HNO_3 > H_3PO_4 > H_3AsO_4 > H_3SbO_4$.

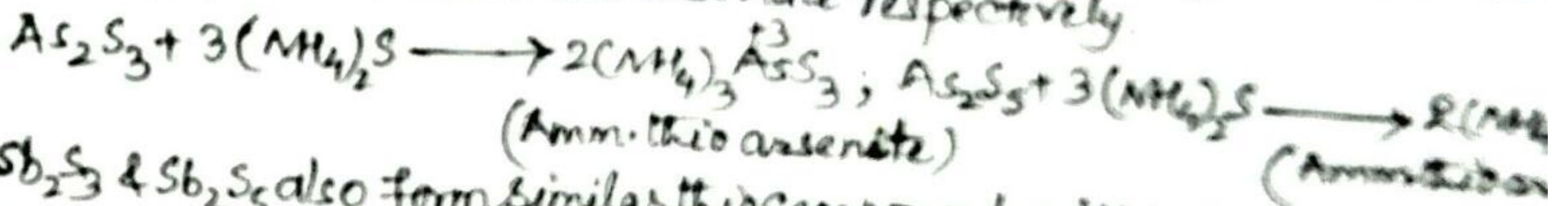
The strength & stability of oxyacids of an element increases on increase in its oxidation states, e.g. $HNO_3 > HNO_2$.

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



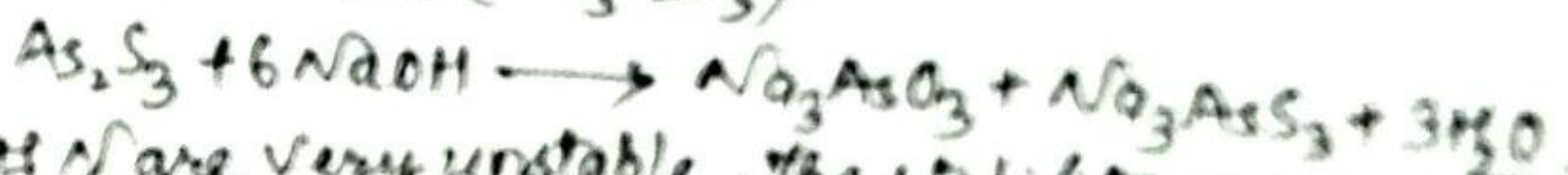
All the pentoxides react with alkalis giving salts.
 e.g.; $N_2O_5 + 2NaOH \rightarrow 2NaNO_3 + H_2O$ (Sodium nitrate); $P_2O_5 + 6NaOH \rightarrow 2Na_3PO_4 + 3H_2O$ (Sod Orthophosphate)

6. Formation of Sulphides: All elements of Gr. 15 (except N) form sulphidic 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 arsenite 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 N to Bi. The three elements of Gr. 15 (i.e., As, Sb & Bi) form all precipitate hydrogen sulphide (H_2S) gas from their salts solution in acidic medium.

