



# THE IIT - JEE SECRET

JEE MAINS AND JEE ADVANCED

INORGANIC CHEMISTRY  
VOL - II



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## P – Block ( 15, 16, 17, 18 Group)

G7P-15

### NITROGEN FAMILY

(pnictogens / pnictogens)

→ Atmosphere :  $N_2(g) = 78\%$ .

$O_2(g) = 21\%$ .

$Ar = 1\%$ .

Earth crust

Oxygen = 46.6 %.

Silicon = 27 %.

Al = 8.4 %.

Fe = 5 %.

N  
P  
As

Sb  
Bi

① Electronic configuration -  
 $ns^2 np^3$       5 valence electrons

7 N      [He]       $2s^2 2p^3$

15 P      [Ne]       $3s^2 3p^3$

33 As      [Ar]       $3d^{10} 4s^2 4p^3$

51 Sb      [Kr]       $4d^{10} 5s^2 5p^3$

83 Bi      [Xe]       $4f^{14} 5d^{10} 6s^2 6p^3$

② Atomic size :-

Increases down the group (no exception)

③ Ionisation energy :-

Decreases down the group.

④ EN

Generally decreases down the group

N 3.0

P 2.1

As 2.0

Sb 1.9

Bi 1.9

EN of Bi, is equal to the EN of the Sb because more diffused F-Orbitals present before Valence Shell in Bi.

⑤ Density :-

$$d = \frac{\text{mass}}{\text{vol}^m}$$

Density increases down the gp in N<sub>2</sub> family.  
bcz at mass much ↑ in comparison to atomic vol<sup>m</sup>.

⑥ Metallic Nature -

Metallic nature increase down the gp.

N	
P	
As	→ diagonal
Sb	
Bi	

→ In this family N, P are non metals

→ As, Sb are metallioids

→ Bi is metal

⑦ Atomicity - (No of atoms in their molecular)

Atomicity of nitrogen is 2, ∴ diatomic  
Molecule

N → 2 diatomic

P → 2 diatomic

AS → 4 tetraatomic

Sb → 4 tetraatomic

Bi is metallic in nature

## Allotropy -

Except nitrogen all are allotropic in nature

(g) Oxi<sup>n</sup> state and Covalency → no. of covalent bonds formed by element  
 or Valency

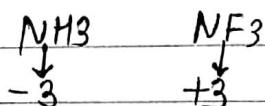
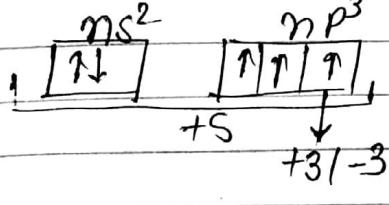
The highest covalency is 4 of element of second period bcz 4 orbitals (namely  $1 \rightarrow 2 S$ ,  $3 \rightarrow 3 P$ ) are present in their valence shell.

Therefore element of 2<sup>nd</sup> period cannot expand their octet.

⇒ The elements of higher period, expand their octet and their co-valency because vacant d-orbitals present in their valence shell.

Example -  $PCl_5 \rightarrow$  5 covalency of P, Oxi<sup>n</sup>st = +5  
 $PF_6 \rightarrow$  6 covalency of P Oxi<sup>n</sup>st = +5

⇒ Common Oxi<sup>n</sup> state of pnictogens is +3, -3 +5



⇒ The stability of -3 Oxi<sup>n</sup> state decreases down the gp because increases metallic nature of the element.

⇒ The stability of +5 Oxi<sup>n</sup> state also decreases down the group due to inert pair effect and hence +3 Oxi<sup>n</sup> state becomes more stable down the group.

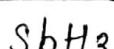
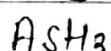
→ The oxidation state of nitrogen & phosphorous vary from -3 to +5

$\text{NH}_3 \rightarrow -3$	$\text{N}_2 \rightarrow 0$	$\text{NO}_2 \rightarrow +4$
$\text{NH}_2\text{-NH}_2 \rightarrow -2$	$\text{N}_2\text{O} \rightarrow +1$	$\text{N}_2\text{O}_5 \rightarrow +5$
$\text{NH}_2\text{-OH} \rightarrow -1$	$\text{NO} \rightarrow +2$	
	$\text{N}_2\text{O}_3 \rightarrow +3$	

## COMPOUNDS

① Hydrides - binary compound of hydrogen are known as hydrides

② General formula of hydrides of pnictogens is  $MH_3$ ,



Q) pnictogens form trihydrides with hydrogen not pentahydrides Explain?

Ans For N → absence of vacant d-orbitals in nitrogen. In other pnictogens d-orbitals are much diffused & hence effective overlapping does not take place b/w 1s orbital of hydrogen and hence they do not form pento oxides.

② Stability of trihalides :-

Stability decreases down the group.

Stability means Value of Bond Energy.  
 These hydrides are covalent in nature & covalent bond is formed by process of overlapping & for effective overlapping, orbitals are less diffused & min energy diff b/w them therefore stability of hydrides decrease down the group.

Stability of hydrides decreases in S-block also but explanation diff. in S-block, ionic hydrides (depends on LE)  $LE \propto \frac{q_1 q_2}{r_1 + r_2}$

$MH_3$	Stability	Bond energy	Red <sup>n</sup> nature	MP/BP
$NH_3$				
$PH_3$				
$AsH_3$	dec	dec	inc	
$SbH_3$				
$BiH_3$				

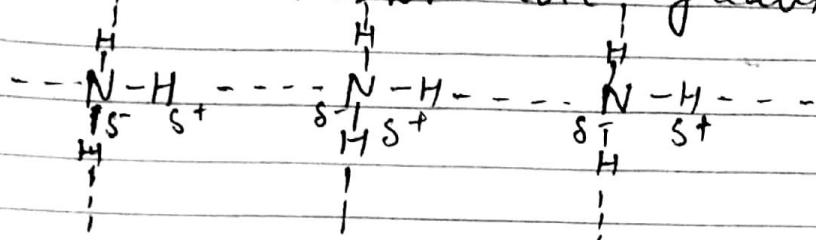
Reducing nature ↑, bcz decreases BE, more easy to give  $H_2$

### ③ MP/BP

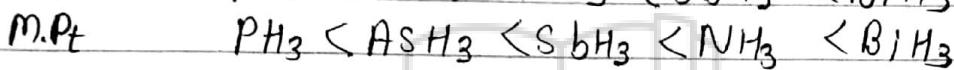
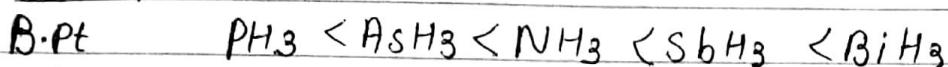
They are covalent molecule hence van der waal's attraction forces exist b/w molecules.

They become more effective on rising surface area & molecular mass. and hence MP/BP of hydrides are generally increases down the group

Hydrogen bond exists b/w  $\text{NH}_3$  molecules & hence, its MP/BP are, greater than expectation.



Exact order -



(4) Basic nature -

Basic nature ↓ down the gp of hydrides.

Reasons:-

1. Except Nitrogen other central atom contains Vacant d-orbitals and they are electrophilic in nature as well as their diffuse nature the ep of e- of central atom is not easily available for Lewis acid and hence decreases their basic strength.

2. The bond angle of  $\text{NH}_3$  is  $107^\circ$  but bond angle of other hydrides is nearly  $90^\circ$ . It means  $\text{NH}_3$  is formed by the process of hybridisation & lp exists in  $\text{sp}^3$  hybrid orbitals.

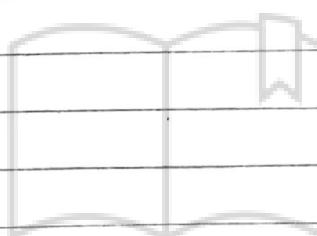
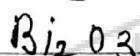
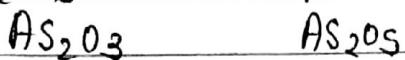
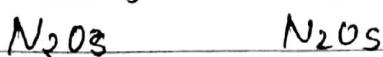
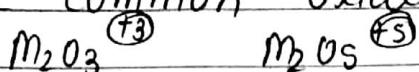
But other hydrides are formed by the overlapping of pure p-atomic orbitals & s-orbital of Hydrogen and hence lp present in their pure s-orbitals  $\text{sp}^3$  hybrid orbital is more directional in comparison to

S - orbital + make a stronger bond and hence  $\text{NH}_3$  is stronger base

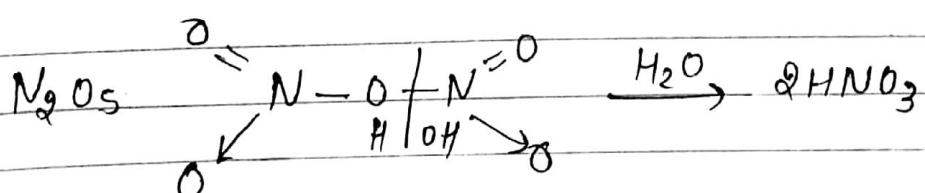
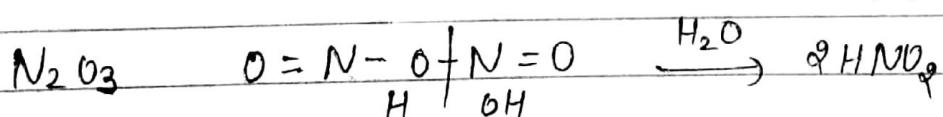
## (2) Oxides:-

nonmetals react with oxygen + form oxides.

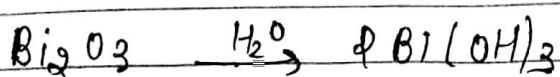
The common oxides are -  $\text{M}_2\text{O}_3$  +  $\text{M}_2\text{O}_5$



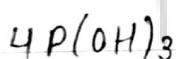
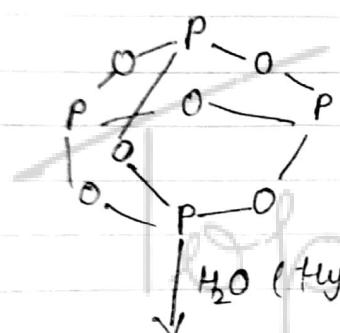
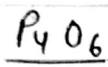
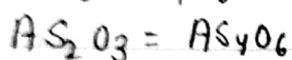
①  $\Rightarrow$  penta oxides are more covalent than trioxides & hence they are more acidic than trioxide.



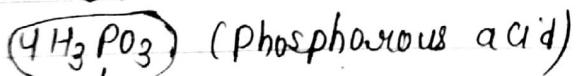
② Bismuth oxide is ionic in nature and hence it is a basic oxide.



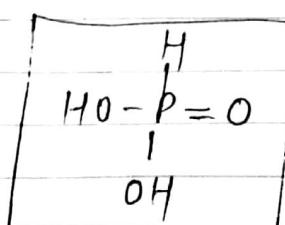
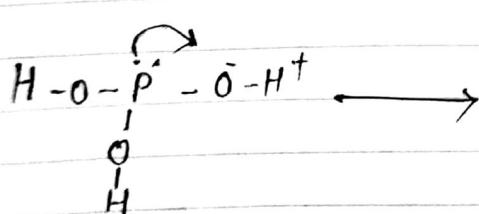
③ Oxides of P Arsenic & antimony exists in their dimorphic form



or

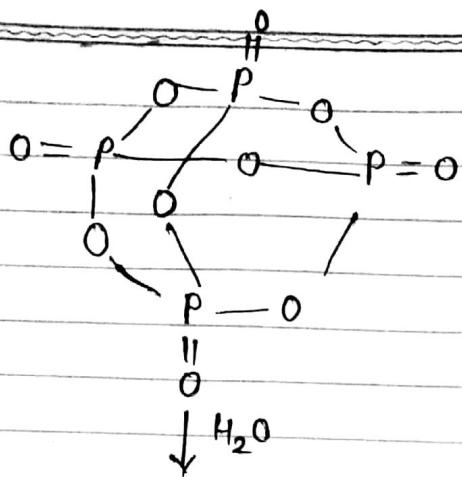


can give 2H

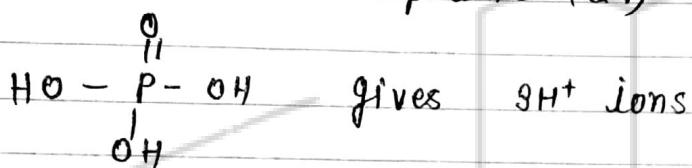


∴ dibasic acid





$H_3PO_4$  (Phosphoric acid)



Similarly for As + Sb

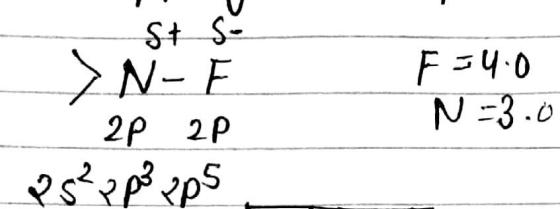
- ④ Stability decreases down the group of covalent oxides. (not compare with Bi) (effective overlapping)  
 $\Rightarrow$  penta oxides are more stable than trioxides.
- ⑤ All penta oxides are acidic trioxides of N + P are also acidic trioxides of As + Sb are amphoteric but bismuth trioxide is basic in nature

### ③ Halides -

- ① Common halides are  $MX_3$  &  $MX_5$
- ② Due to absence of valence d-orbitals N does not form pentahalides.  
 only  $NF_3$  is stable halide of Nitrogen.

Reason  $\Rightarrow$  F is higher EN element than Nitrogen & hence sufficient polarity present in N-F bond as well as less energy difference b/w the

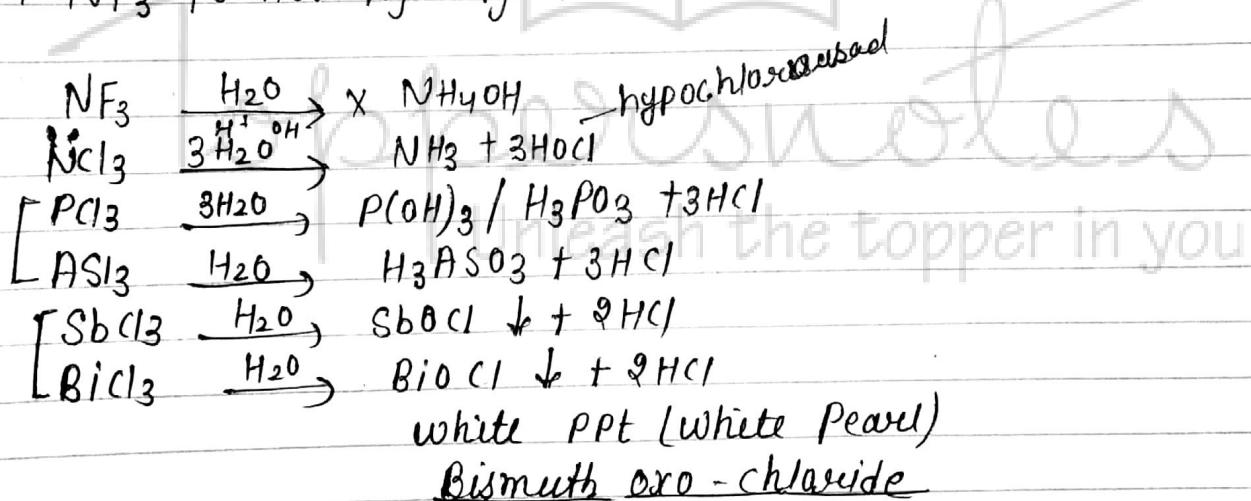
Orbitals of Nitrogen & Fluorine & hence effective overlapping takes place.



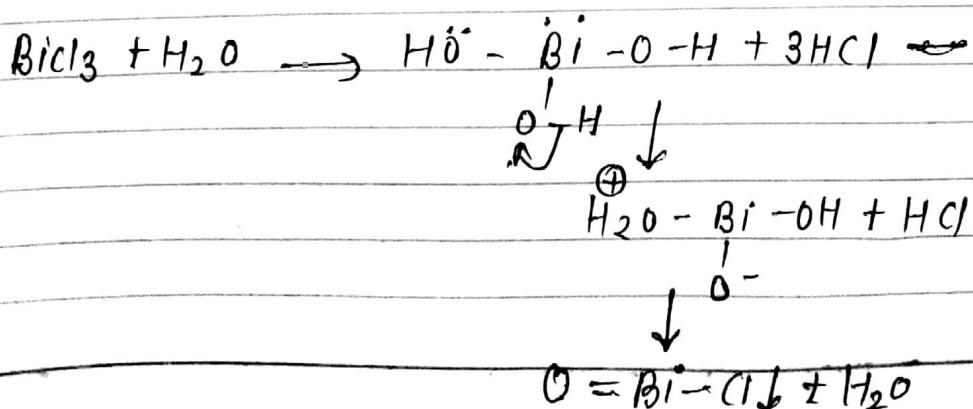
(3) Pentahalides are more covalent than trihalides

(4) Hydrolysis of trihalides

\*  $\text{NF}_3$  is not hydrolysed

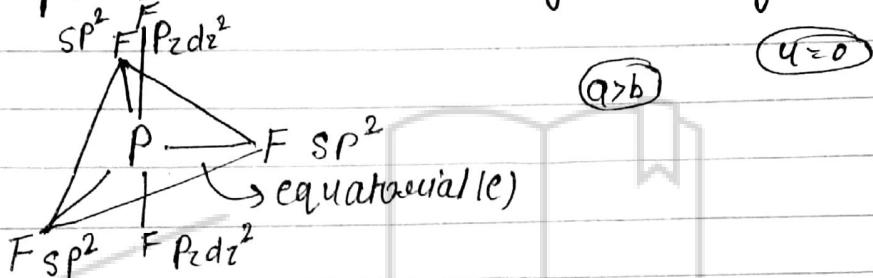


Formation of BiOCl

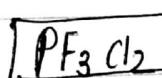


- ⑤ PFs PCl<sub>5</sub> PBr<sub>3</sub> PI<sub>5</sub> ( ) → less stable  
ASFs (ASCl<sub>5</sub>) P → all are known  
SbFs (SbCl<sub>5</sub>)  
BiF<sub>5</sub>

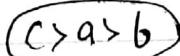
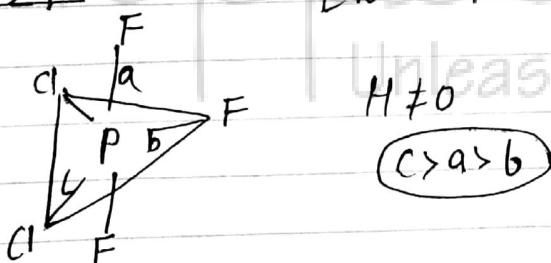
- ⑥ All pentahalides are trigonal bipyramidal



Axial bonds are longer than equatorial.

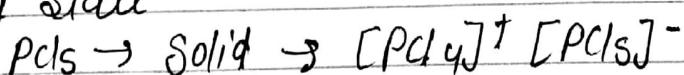


[Bent's Rule : Higher EN at axial position]

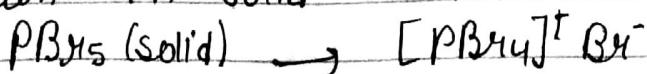


compare axial equatorial  
only when same atoms.

- ⑦ PF<sub>5</sub> is a covalent and hence trigonal bipyramidal structure in gaseous liquid & solid state  
But PCl<sub>5</sub> contains tetrahedral & octahedral ions in solid state.



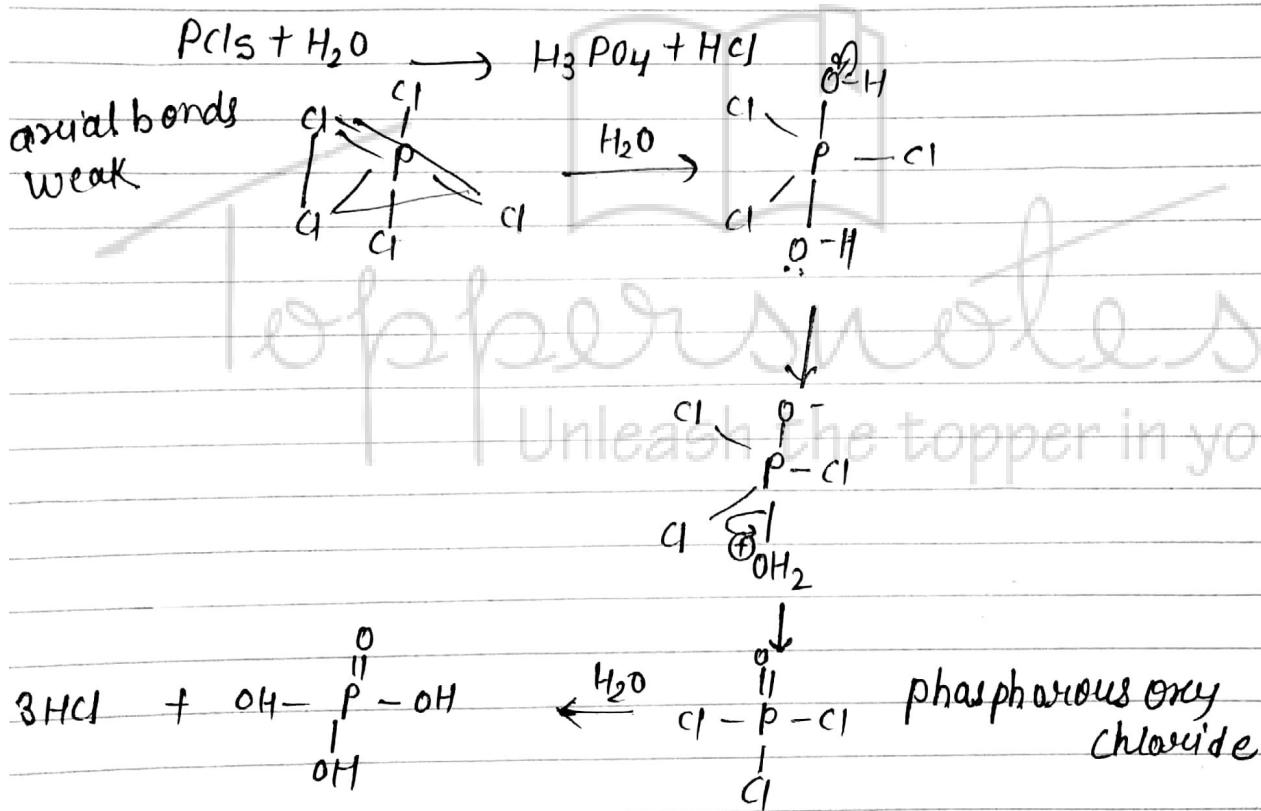
PBr<sub>3</sub> is trigonal bipyramidal in gaseous & liquid state but contains tetrahedral Cation & bromide ion in solid state.



$\text{PI}_5$  is trigonal bipyramidal in gaseous state  
It contains tetrahedral cation of iodide anion in  $\text{SOI}^n$  state and it does not exist in solid state.

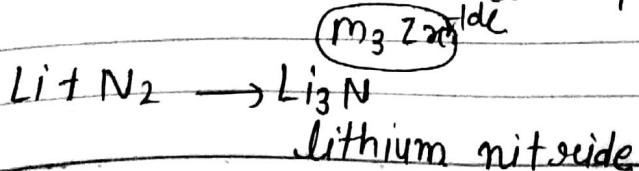


- ⑧ Am Rentahalides change into their corresponding oxyacids on hydrolysis



## REACTION WITH METALS

They form binary compounds with metal in which ox. st. of pnucogens is -3



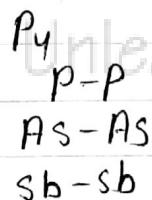
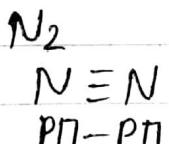
## ANOMALOUS PROPERTIES OF NITROGEN

- ① Due to smaller size
- ② Higher EN
- ③ Higher IP
- ④ Absence of vacant d-orbitals

the properties of nitrogen are not similar to the properties of other elements in their group

for exp -

① Nitrogen is a diatomic molecule & make  $\text{p}\pi-\text{p}\pi$  bond b/w the atoms in their molecule but other elements are form single bond b/w their atoms in their molecule.

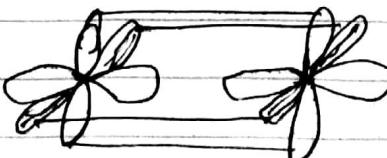


Reason: Due to smaller size of nitrogen its atomic orbitals are less diffused & hence effective overlapping takes place b/w them & hence 1σ and 2π-bonds present b/w the atoms in  $\text{N}_2$  Molecule.

The bond enthalpy of nitrogen is highest among all homo diatomic molecules and hence  $\text{N}_2$  is nearly inert at ordinary conditions. ∴ it exists highest in atmosphere.



941.5 KJ/mole



- ② Cannot expand their octet.
- ③ Highest covalency of nitrogen is 4.

## COMPOUNDS OF NITROGEN

### DINITROGEN ( $N_2$ )

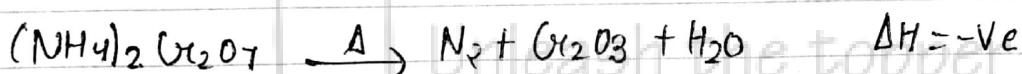
Preparation -

#### (i) Late Method -

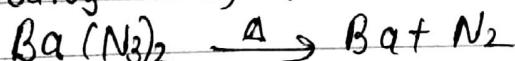
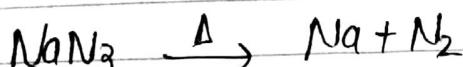
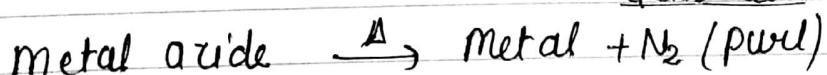


#### (ii) Other methods -

##### (a) Decomposition of ammonium salts -



##### (b) Decomposition of metal azides -



### Properties

- ① colourless & odourless gas.
- ② Sparingly soluble in water
- ③ Due to higher bond enthalpy,  $N_2$  acts as a inert gas at ordinary conditions.