Nitrogen Family | (VA)

N, P — Non metal

@ News paper aaj sab bik गया |.

As, Sb — Metalloid → also called pnicogens.

Bi — Metal

* **Occurence:** N → N_2 (gas) only gas. $\boxed{B.pt \rightarrow O_2 > N_2}$

P → P_4 (solid)

→ Nitrogen is small in size so more overlapping & strong $p\pi$-$p\pi$ bond.

N_2 ..... N_2 ..... N_2 O_2 ..... O_2 ..... O_2

↳ vanderwaals force of attraction

↳ instantenous dipole ~~moment~~ induced dipole.

↳ dispersion force | london force.

→ N_2 → 78% in air. → O_2 → 21% in air.

→ $N \equiv N$

↳ Bond dissociation energy is very high.

② **General configuration:-** $ns^2\ np^3$.

③ **Size:-** N, P, As, Sb, Bi ↓ size ↑ 55%.

↓ size ↑es 5%.

↳ because of lanthanide contraction.

$\boxed{\text{in some books, size of Sb} \simeq \text{Bi}}$

④ **Oxidation state:-** −3 to +5.

e.g. $\overset{-3}{N}H_3$ $\overset{+5}{N_2}O_5$

N^{-3} → nitride,

P^{-3} → phosphide.

~~ex.~~ PCl_5 exist but NCl_5 doesnot exist.

↳ due to absence of vacant d-orbital.

N, P, As, Sb, Bi → $N^{+5} > N^{+3}$

$P^{+5} > P^{+3}$.

stability of +5 O.S ↓es but stability of +3 O.S ↑

due to inert pair effect.

Bi → Bi^{+3}

Bi^{+5} → $Bi^{+3} > Bi^{+5}$.

• **Oxidizing power** → $As^{+5} < Sb^{+5} < Bi^{+5}$

$Bi^{+5} \xrightarrow{+2e^-} Bi^{+3}$

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→ ~~Oxidizing power~~ → $N^{+3} < P^{+3} < As^{+3} < Sb^{+3} < Bi^{+3}$
Stability

5. Ionization energy:-

$I.E \propto \frac{1}{R}$. $N > P > As > Sb > Bi \rightarrow I.E$

6. Electro negativity

$E.N \propto \frac{1}{R}$ $N > P > As > Sb > Bi \rightarrow E.N.$

7. Electron affinity

$P > N > As > Sb > Bi$

8. Density:- top to bottom, m ↑es, density ↑es.

$N < P < As < Sb < Bi$

9. Non-metallic character:-

$\propto E.N.$

N
P
As
Sb
Bi

Non-metallic character ↓s
Metallic character ↑es.
↳ readily lose e^-

Q. Non-metallic character को decreasing order;-

N S O P

$\propto E.N.$ ↳ $O > N > S > P$.

Chemical properties

1. Reaction with H_2:-

$M + H_2 \rightarrow MH_3$.

NH_3, PH_3, AsH_3, SbH_3, BiH_3.

a. Bond length:-

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

b. Bond dissociation energy

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

c. Basic strength

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

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$\rightarrow NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
(weaker - bond)

Nitrogen

preparation

① By distillation of air

Q. Which compound on heating does not evolve N_2?

(a) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + H_2O$ (green color)

(b) $NaN_3 \xrightarrow{\Delta} Na + 3/2\,N_2$

(c) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$ (pure nitrogen) (Barium azide)

(d) $NH_4.NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$ (ammonium nitrite)

(e) $NH_4.NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ (amm nitrate; oxide)

$\rightarrow Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$ (Barium azide)

properties

→ Nitrogen is less reactive than phosphorus due to high B.D.E.

① $N_2 + O_2 \xrightarrow[\Delta]{2000^\circ C} 2NO$ (nitric oxide)

② $N_2 + Li \xrightarrow{\Delta} Li_3N$ (only IA)

③ $Be + N_2 \xrightarrow{\Delta} Be_3N_2$.

Q. Which element form nitride when heated with N_2?

(a) Li (b) Ba (c) Al (d) All

Q. Which metal does not form nitride when heated with N_2?

(a) Li (b) Ba (c) Al (d) Na

Rxn

$Na + N_2 \xrightarrow{\Delta}$ No rxn

$Na + NH_3 \longrightarrow NaNH_2 + H_2$ (sod. amide)

$Na + N_3H \longrightarrow NaN_3 + \frac{1}{2}H_2$ (Hydrazoic acid)

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PH_3 (Phosphine)

preparation

① $Ca_3P_2 + 3HOH \longrightarrow \underset{\text{Ca(OH)}_2}{3Ca(OH)_2} + \underset{\text{phosphine}}{2PH_3}$

$Ca_3P_2 + \text{dil. HCl} \longrightarrow CaCl_2 + PH_3$
Cal. phosphide.

lab preparation :-

$P_4 + NaOH \xrightarrow{\Delta} \overset{-3}{PH_3} + Na\overset{+1}{H_2}PO_2$
white phosphorus — Sodium Hypo phosphite

$PH_3 + O_2 \longrightarrow$ white fumes P_2O_5 or P_4O_{10}
phosphine, air — (vortex ring)

Note :- pure PH_3 → non-flammable
impure PH_3 → Flammable / Inflammable · due to impurity of P_2H_4.

Rxn :

$P_4 + NaOH \longrightarrow PH_3 + NaH_2PO_2$

$PH_3 + HI \longrightarrow PH_4I$
crystal

$PH_4I + KOH \longrightarrow KI + PH_3$
base — pure

Other methods

→ $\overset{+3}{Al}\overset{-3}{P} + HOH \longrightarrow Al(OH)_3 + PH_3$.

→ $H_3PO_3 \xrightarrow{\Delta} PH_3 + H_3PO_4$

→ $H_3PO_2 \xrightarrow{\Delta} PH_3 + H_3PO_4$.

properties

→ Colorless gas with rotten fish smell. & highly poisonous.
→ It explodes in contact with traces of O.A e.g. conc. HNO_3, Cl_2 & Br_2 vapour
→ It is slightly soluble in water.

Q. Which of the following has rotten fish smell?
(a) H_2S (rotten egg) (b) SO_2 (suffocating smell of burning sulphur.) (c) PH_3 (d) None

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→ H_3PO_2 → Hypophosphorous acid (phosphinic acid)
→ H_3PO_3 → phosphorous acid (phosphonic acid).

Q. What are the mixture used in Holme's signal?
(a) Ca_3P_2 (b) CaC_2 ~~(c)~~ $Ca_3P_2 + CaC_2$ (d) None

$$Ca_3P_2 + HOH \longrightarrow Ca(OH)_3 + PH_3 \leftarrow \text{flamable}$$

$$CaC_2 + HOH \longrightarrow Ca(OH)_2 + CH \equiv CH$$

→ smoke's screen → $Ca_3P_2 + CaC_2$

→ Fossy jaw is related to white phosphorus.

NH_3 (Ammonia)

preparation

① Haber's process :-

$$N_2 + 3H_2 \xrightarrow[\text{Mo (promoter)}]{\text{Fe (catalyst)}} 2NH_3$$

→ endothermic $\Delta H = -ve$.
→ High pressure & low temperature.

② Hydrolysis of Urea

$$NH_2(H)-C(=O)(OH)-NH_2(H) \longrightarrow 2NH_3 + H_2CO_3 \text{ unstable}$$

$$H_2CO_3 \rightarrow H_2O + CO_2$$

③ Hydrolysis of calcium cyanamide

$$\overset{+2}{Ca}\overset{-2}{CN_2} \xrightarrow{HOH} \text{urea} \xrightarrow{HOH} NH_3$$

CN_2^{-2}
↓
$N=C=N^-$ ← linear

CN_2^{-2} & CO_2 are isostruct
↳ isoelectronic ...

④ Hydrolysis of Nitride

$$Mg_3N_2 \xrightarrow{HOH} 2NH_3 + 3Mg(OH)_2$$

$$Ca_3N_2 \xrightarrow{HOH} 2NH_3 + 3Ca(OH)_2$$

Q. Which compound on hydrolysis form ammonia?
(a) urea (b) cynamide (c) nitride ~~(d)~~ All

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Q. In which rxn PH_3 not formed?

(a) ALP $\xrightarrow{HCl} PH_3 + AlCl_3$ (b) $Ca_3P_2 \xrightarrow{HOH} PH_3 + Ca(OH)_2$

(c) $H_3PO_3 \xrightarrow{\Delta} PH_3 + H_3PO_4$ (d) White P $\xrightarrow{NaOH} PH_3 + NaH_2PO_2$

(e) Red P $\xrightarrow{NaOH}$ No rxn.

disproportionation rxn

property of NH_3

(1) **Lewis base:-** Due to presence of lone pair.

$NH_3 + H^+ \longrightarrow NH_4^+$

$PH_3 + H^+ \longrightarrow PH_4^+$

$NH_3 > PH_3$ — Basicity. ↓ Basic les

(2) Thermal stability → $NH_3 > PH_3$

(3) **Reducing character:-**

HF	HCl	HBr	HI
H_2O	H_2S	H_2Se	H_2Te
NH_3	PH_3	AsH_3	SbH_3

→

Size ↑as, Bond length ↑es

B.D.E ↓es, T.S ↓es.

Reducing character ↑es

(3) $NH_3 + Cl_2 \longrightarrow \underset{\text{explosive halide}}{NCl_3} + HCl$

(Cl_2 excess)

$NH_3 + Cl_2 \longrightarrow N_2 + NH_4Cl$

(NH_3 excess)

Note:- Moist NH_3 can be dried over quick lime (CaO).

$CaO + H_2O \longrightarrow Ca(OH)_2$

but it can't be dried over $CaCl_2$, H_2SO_4, P_4O_{10}.

$CaCl_2 + NH_3 \longrightarrow CaCl_2 \cdot 8NH_3$

$H_2SO_4 + NH_3 \longrightarrow (NH_4)_2SO_4$

$P_4O_{10} + NH_3 \longrightarrow (NH_4)_3PO_4$

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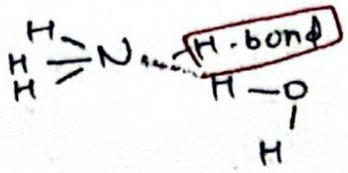
Reactions

① $NH_3 + O_2 \xrightarrow{\Delta} N_2 + H_2O$

② $NH_3 + O_2 \xrightarrow[350^\circ C]{Pt} NO + H_2O$ (Ostwald process)

③ $NH_3 + CO_2 \xrightarrow[\Delta]{\text{high Pr.}} NH_2CONH_2$
urea

④ NH_3 dissolve in H_2O due to H-bond formation.



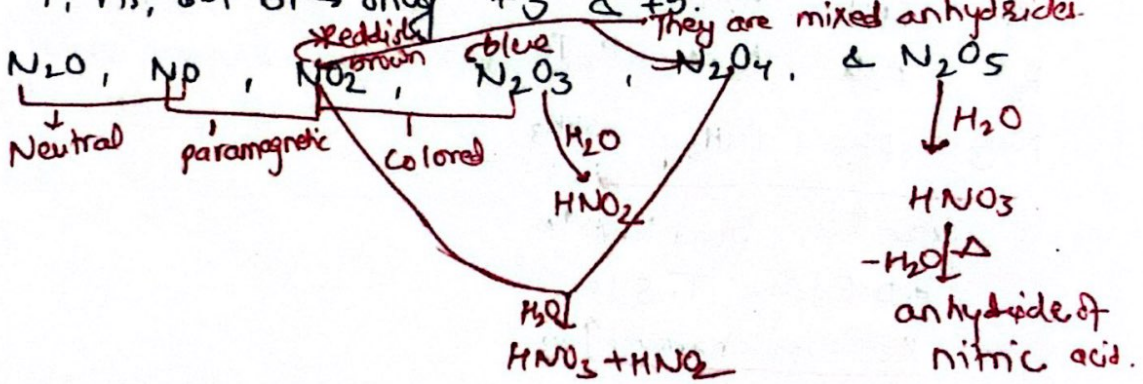
Oxides of Nitrogen

— CO, N_2O & NO are neutral oxides in whole chemistry.

→ Nitrogen forms various types of oxides ranging from +1 to +5 O.S.

→ P, As, Sb, Bi → only +3 & +5.

→ N_2O, NO, NO_2, N_2O_3, N_2O_4, & N_2O_5 — they are mixed anhydrides.



① N_2O (

str.

$N \equiv N \rightarrow O$

$N \equiv \overset{\oplus}{N} - \overset{\ominus}{O}$

sp, linear, 180° — bond angle.

dipole moment ≠ 0
↳ polar molecules

property – Neutral
– Involuble in H_2O
– +1 O.S
– Diamagnetic

- colorless
- also called laughing gas.
- used as anesthetic

Methods of prepr

→ $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$
ammonium nitrate

but, $\boxed{NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O}$
amm. nitrite.

② NO (Nitric oxide)

str → $\overset{\odot}{N}=\ddot{O}$

→ unpaired electron → 1 (so, paramagnetic)
→ odd e^- molecules.

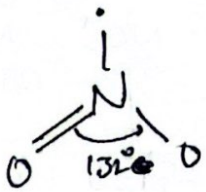
prp $N_2 + O_2 \xrightarrow{2000°C} 2NO$

Test of NO
↳ gives brown ring with aq. $FeSO_4$.

$[Fe(H_2O)_6]SO_4 \xrightarrow{NO} [Fe(H_2O)_5\overset{+}{N}O]SO_4$.

③ NO_2 (

str → $O=N\cdot$ (↓ O)



→ sp^2 hybridization
→ unpaired electron = 1, so paramagnetic
→ Reddish brown color.
→ Bond angle → 132°, angular

④ N_2O_4

str → $O=N$ (↓ O) —— $N=O$ (↓ O)

→ sp^2, planar.
→ unpaired e^- (η) = 0
→ Diamagnetic

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→ NO_2 & N_2O_4 are mixed anhydride.

$\overset{+4}{N_2O_4} \mid \overset{+4}{NO_2} \xrightarrow{H_2O} \overset{+5}{HNO_3} + \overset{+3}{HNO_2}$

⑤ N_2O_3

str → $O=\underset{\downarrow}{\underset{O}{N}}-N=O$

$N_2O_3 \rightarrow NO + NO_2$ → blue color.
↳ N_2O_3.
1 : 1

$N_2O_3 \underset{\Delta, -H_2O}{\overset{H_2O}{\rightleftharpoons}} HNO_2$

N_2O_3 ↓ anhydride of nitrous acid

⑥ N_2O_5

str → $O=\underset{\downarrow}{\underset{O}{N}}-O-\underset{\downarrow}{\underset{O}{N}}=O$

– There is no $N \equiv N$ bond.

→ N_2O_5 (s) → NO_2^+ NO_3^- (nitronium nitrate)
↓ ionic solid

NO_2^+: $O=\overset{\oplus}{N}=O$
sp, linear
BA = 180°

NO_3^-: $O=\underset{\downarrow}{N}-O^-$
O^-
↳ sp^2, planar, BA → 120°

Q. Which compound when dissolved in H_2O, no effect on litmus?
~~(a)~~ N_2O (b) NH_3 (c) CaO (d) PH_3 (e) SO_3

→ $N_2 + O_2 \longrightarrow 2NO$.

$2NO + O_2 \longrightarrow 2NO_2$
~~reddish brown~~ ↳ after sometime color disappear due to dimerization & form N_2O_4.

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Fertilizer (N, P & K)

① Nitrogenous:-

ⓐ Urea
ⓑ $(NH_4)_2SO_4$
ⓒ Nitrolim

$\xrightarrow{H_2O}$ NH_3 → useful for plant

- Urea is better than $(NH_4)_2SO_4$.

$$\underset{H}{NH_2}\text{)}\underset{OH}{-}\overset{O}{\overset{\|}{C}}\underset{H}{(NH_2} \longrightarrow \underset{\text{Taken by plant}}{2NH_3} + H_2O + CO_2 \uparrow$$

$$\underset{\text{makes soil acidic}}{(NH_4)_2SO_4} \xrightarrow{HOH} NH_3 + \underset{\text{acidic}}{H_2SO_4}$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO \xrightarrow{C,\ \Delta} CaC_2 + CO$$

$$CaO + \underset{RA}{C} \xrightarrow{\Delta} Ca + CO \ \times$$

$$CaO + C \xrightarrow{\Delta} CaC_2 + CO$$

$$\xrightarrow{\text{hydrolith}\ N_2} \boxed{CaCN_2 + C}$$

↳ Nitrolim

② Phosphatic fertilizer

e.g. Thomas slag:- waste product of ~~steel~~ steel industry.

$$\underset{\text{ore}}{Fe_2O_3} \xrightarrow[\Delta]{C} 2Fe + 3CO$$

+

$$\underset{\text{impurity}}{SiO_2 / P_2O_5} \xrightarrow{CaCO_3} \boxed{CaSiO_3 + Ca_3(PO_4)_2} \rightarrow \text{Thomas slag}$$

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PX_3 :- phosphorus Halide

PX_3 PX_5.

X = F, Cl, Br, I.

Note :- PI_5 (g) does not exist due to steric crowding.

PX_3

preparation

① By passing dry chlorine over heated white phosphorus.

$$P_4 + Cl_2 \longrightarrow PCl_3$$

② By the action of thionyl chloride with white phosphorus.

$$P_4 + SOCl_2 \longrightarrow PCl_3 + SO_2 + S_2Cl_2.$$

properties

① PCl_3 is colorless oily liquid.

② $PCl_3 + HOH \longrightarrow H_3PO_3 + HCl$

③ It react with organic compound.

$$RCOOH + PCl_3 \longrightarrow RCOCl + H_3PO_3$$

$$ROH + PCl_3 \longrightarrow RCl + H_3PO_3$$

PCl_5

preparation

① P_4 (white) + Cl_2 (excess) $\longrightarrow PCl_5$.

② $P_4 + SO_2Cl_2 \longrightarrow PCl_5 + SO_2$

sulphuryl chloride

properties

① PCl_5 is yellowish white powder.

② $PCl_5 + HOH \longrightarrow H_3PO_4 + HCl$

③ When heated, it sublimes but decompose on strong heating.

$$PCl_5 \xrightarrow[\text{strong heat}]{\Delta} PCl_3 + Cl_2$$

→ $PCl_5 + RCOOH \longrightarrow RCOCl + POCl_3 + HCl$

→ $PCl_5 + ROH \longrightarrow RCl + POCl_3 + HCl$.

HNO_3
└ called → aqua fortis (strong H_2O)

→

preparation

① Birklend Eyde process (old method)

$$\rightarrow N_2 + O_2 \xrightarrow[\text{electric arc}]{2000^\circ C} NO \xrightarrow{O_2} NO_2 \xrightarrow{H_2O} HNO_3 + HNO_2$$

NO_2: acidic oxide

$HNO_2 \xrightarrow{\Delta} HNO_3 + NO$ → recycle

2000°C — due to break N_2 & O_2 bond

we need high B.D.E

Q. Which oxide does not form acidic solution with water?

(a) $N_2O_3 \xrightarrow{HOH} HNO_2$

(b) $N_2O_5 \xrightarrow{H_2O} HNO_3$

(c) NO_2 (d) N_2O_4 ~~(e)~~ N_2O ~~(f)~~ NO

$NO_2 \xrightarrow{HOH} HNO_3 + HNO_2$

② Ostwald method (Modern method)

$$4NH_3 + 5O_2 \xrightarrow[\text{catalyst } 550K]{Pt/Rh} 4NO + 6H_2O$$

$$4NO \xrightarrow{O_2} NO_2 \xrightarrow{HOH} HNO_3 + HNO_2$$

$HNO_2 \xrightarrow{\Delta} HNO_3 + NO$ ← recycle.

properties

① Nitrating mixture :- conc. HNO_3 + conc. H_2SO_4.

conc. HNO_3 → base; conc. H_2SO_4 → acid

NO_2^+ ← Electrophile

② Oxidizing agent :- conc. HNO_3 oxidizes non-metal to oxy acid.

oxy acid → max. O.S.

e.g. C, S, P, I_2 $\xrightarrow{\text{conc. } HNO_3}$ CO_2 (↓ HOH → H_2CO_3), H_2SO_4, H_3PO_4, HIO_3 (← not in HIO_4)

→ maximum metal soluble in conc HNO_3 but Au/Pt (Noble metal) are only soluble in aqua-regia.
└ conc HNO_3 + conc HCl
1 : 3

Note: Au soluble in aqua-regia due to oxidation by chlorine.

Conc. HNO_3 + conc HCl
└ nascent Cl^- └ oxidizes

Rxn
$Au \xrightarrow{3Cl} AuCl_3 \xrightarrow{HCl} H[AuCl_4]$ soluble complex.
$Pt \xrightarrow{4Cl} PtCl_4 \xrightarrow{2HCl} H_2[PtCl_6]$ soluble complex
→ act as acid.

→ Be, Al (Al_2O_3), Fe (Fe_3O_4) $\xrightarrow{\text{conc } HNO_3}$ Reaction stop after sometime because of passivity
└ because of inert oxide layer formation

Q. conc. HNO_3 store in container of :-
(a) Pb (b) Cu (c) Ca (d) Al

Q. Gold coated Cu kept in :- conc HNO_3 → no visible reaction.

→ HNO_3 (nitric acid) is colorless. but acquire yellow or Reddish brown color when kept in sunlight.
└ decompose & formation of NO_2

$4HNO_3 \xrightarrow{\text{sunlight}} 4NO_2 + 2H_2O + O_2$.

→ Metal + conc. HNO_3 → $M(NO_3)_2 + H_2O + NO_2$
O.A
Metal nitrate
↓ reddish brow

- Metal + dil. HNO_3 → $M(NO_3)_2 + H_2O + NO$
O.A
↓ nitric oxide

Eg. conc HNO_3 + Pb, Cu, Ag, Hg, Fe, Zn $\longrightarrow$ NO_2 + M nitrate.

but with Sn $\longrightarrow$ H_2SnO_3
meta stannic acid.

- dil. HNO_3 + Pb, Cu, Ag, Hg $\longrightarrow$ NO + $M(NO_3)_2$

but Fe & Zn $\longrightarrow$ N_2O + ..

- very dil. HNO_3

+ Mn / Mg $\longrightarrow$ H_2 + $M(NO_3)_2$

but Fe, Zn, Sn $\longrightarrow$ NH_4NO_3 + ..

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