G-15 Elements:- (Nitrogen Family):- P-Block

1. N, P, As, Sb, Bi (pnicogens) and Mc (Moscovium)

Hydrides of these elements cause suffocation

General characteristics:-

1. Electronic confg:-

Element	Atomicity	At. No	Phy. state	$\bar{e}$ nic confg
N	2 (N_2)	7	gas	$[He]\ 2s^2 2p^3$
P	4 (P_4)	15	solid	$[Ne]\ 3s^2 3p^3$
As (Arsenic)	4 (As_4)	33	solid	$[Ar]\ 3d^{10} 4s^2 4p^3$
Sb (Antimony)	4 (Sb_4)	51	solid	$[Kr]\ 4d^{10} 5s^2 5p^3$
Bi	1	83	solid	$[Xe]\ 4f^{14} 5d^{10} 6s^2 6p^3$
Mc	1	115	solid	$[Rn]\ 5f^{14} 6d^{10} 7s^2 7p^3$

Note:- (1) In As, Sb, Bi & Mc there are 18 $\bar{e}$s in penultimate shell.

(2) Gen. $\bar{e}$ nic confg :- $ns^2 np^3$

2. Occurence :-

Abundance in Air: $N_2 > P_4 > As > Sb > Bi$

Abundance in earth crust:- $P_4 > N_2 > As > Sb > Bi$

N_2

(1) 78% by volume in air

(2) In earth in the form of nitrates

1. $NaNO_3 \rightarrow$ chile salt peter
2. $KNO_3 \rightarrow$ Indian salt peter.

(3) In the form of proteins in plants & animals

P_4

(1) In bones

(2) 11th most abundant element

(3) In milk & Egg (Phospho proteins present)

(4) Essential component plant & animal matter

(5) Found in apatite family $Ca_9(PO_4)_6 \cdot CaX_2$ ($X = F, Cl, OH$)

Components of phosphate rock:

1. Fluorapatite $\rightarrow 3Ca_3(PO_4)_2 \cdot CaF_2$
2. chloropatite $\rightarrow 3Ca_3(PO_4)_2 \cdot CaCl_2$
3. Hydroxy patite $\rightarrow 3Ca_3(PO_4)_2 \cdot Ca(OH)_2$

Note:- As, Sb, Bi are found mainly as sulphide ores

③ Metallic character :- N → Bi ↑'ses, This is due to → ① ↑'se in size; → ② ↓ in I.E

① N_2, P_4 → Non-metals → Non-conductors of electricity

② As → Metalloid. It is poor conductor

③ Sb → metalloid. It is Good Conductor

④ Bi → metal, " " " "

④ Atomic Radius (Covalent Radius) :- N → Bi ↑'ses

N < P < As < Sb < Bi

70pm, 110, 121, 141, 148 pm

Large difference
Reason :- Greater shielding effect of $2s^2 2p^6$ e's in 'P'

small difference
Reason :- poor S.E shown by $4f^{14}$ e's in Bi

⑤ I.E :- N > P > As > Sb > Bi $\left(I.E \propto \frac{1}{size}\right)$

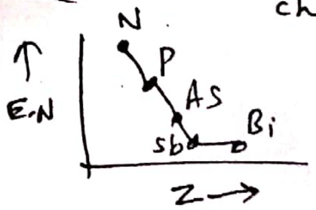
Generally $I_1 < I_2 < I_3 < ..$ (For any element)

I_1 → C < N > O
G-14: C → $2s^2 2p^2$; G-15: N → $2s^2 2p^3$ (stable half filled); G-16: O ($2s^2 2p^4$)

I_2 → N < O > F
G-15: N (After removing 1 e) → $2s^2 2p^2$; G-16: O → $2s^2 2p^3$; G-17: F → $2s^2 2p^4$

⑥ E.N :- N > P > As > Sb = Bi (∵ EN ∝ N.C (OR) Non-metallic character ∝ $\frac{1}{\text{Metallic nature (OR) size}}$)

on pauling scale :- 3.0 2.1 2.0 1.9 1.9



⑦ E.G.E :- (E.A) :- least And N → Bi gradually ↓'ses.

N → +31 kJ/mole due to stable confg

P → −60 kJ/mole

Note :- → ① Non-metal with least −ve EA = P; → ② Non-metal, high −ve EA = Cl

⑧ Allotropy :- Except N_2, all the elements show allotropy

⑨ **M.pts** :- N → As ↑'ses & then ↓'ses

→ As > Sb > Bi > P_4 > N_2 (Highest m.pt = As)

(1089K) (904K) (544K) 317 63K

→ **Reason** :- Highly layered structure of 'As'

⑩ **B.pts** :- N_2 < P_4 < As_4 < Bi < Sb (Highest B.pt = Sb)

(1837K) (1860K)

↓

Bi—Bi metallic bond is weak due to non-participation of $6s^2$ e's in bonding

⑪ **Co-valency** :- It is the no. bonds sharing by atom.

① Gen. C.V = 3

eg:- NH_3, PH_3, PCl_3 etc.

② Maximum Co-valency

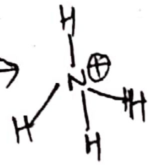
① 'N' = 4

Reason :- Non-availability of d-orbitals (OR) Available of 2s, 2p orbitals

② P, As, Sb etc = 5 (OR) 6 (others)

Reason :- Available of vacant d-orbitals

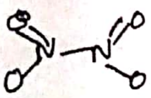
eg ① $NH_4^{\oplus}$ →



① C.V and C.N = 4

② $O.S_N = -3$

③ N_2O_4 →



$C.V_N = 4$ $C.N_N = 3$ $O.S_N = +4$

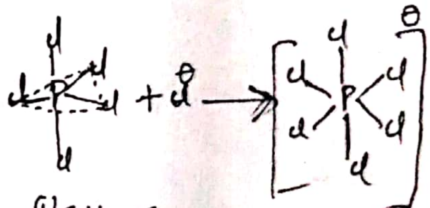
② N_2O_5 →

① $C.V_N = 4$

② $O.S_N = +5$

③ Coordination No = 3

① $PF_6^{\ominus}$ ② PCl_5 ③ $PCl_6^{\ominus}$



① $C.V_p = 5$

② P → sp^3d

③ Trigonal Bipyramidal

④ $C.N_p = 5$

$C.V_p = 6$

P → sp^3d^2

Octahedral

$C.N_p = 6$

⑫ **Oxidation states** :-

① Gen. oxi. states :- −3, +3, +5

−3, +3 → Due to np^3 e's

+5 → Due to participation of $ns^2 np^3$ e's

② Down the grp →

→ ① −3 stability ↓'ses ($\overset{-3}{NH_3}$)

→ ② +3 ,, ↑'ses ($\overset{+3}{BiH_3}$)

→ ③ +5 ,, ↓'ses

③ (Bi) → ① +3 stable

→ ② +5 unstable due to Inert pair effect shown by $6s^2$ e's in Bi

→ ③ BiF_5 known which is ionic ✓

- Due to small size and high E.N, nitrogen exhibits wide range of oxidation states from -3 to $+5$

$$\text{O.S}_N \longrightarrow -3 \quad -2 \quad -1 \quad 0 \quad +1 \quad +2 \quad +3 \quad +4 \quad +5$$

$$\text{Cpd} \longrightarrow NH_3 \quad N_2H_4 \quad NH_2OH \quad N_2 \quad N_2O \quad NO \quad N_2O_3 \quad NO_2 \quad N_2O_5$$

(N_2H_4: Hydrazine)

- In case of 'N', all O.S's from +1 to +4 tend to disproportionate in acidic medium

$$3\overset{+3}{HNO_2} \longrightarrow \overset{+5}{HNO_3} + 2\overset{+2}{NO} + H_2O$$

oxdn: $EW = M/2$

Redn: $E = M/1$

$$EW_{HNO_2} = \frac{M}{2} + M = \frac{3M}{2}$$

$$\therefore nf_{HNO_2} = 2/3$$

$\therefore$ HNO_2 acts as both R.A and O.A

- In case of P_4, all intermediate O.S's disproportionate into +5 and -3 in both acidic & alkali (basic) media

$$4\overset{+3}{H_3PO_3} \longrightarrow 3\overset{+5}{H_3PO_4} + \overset{-3}{PH_3}$$

(H_3PO_3: ortho phosphorous acid) phosphonic acid; (H_3PO_4: ortho phosphoric acid)

oxdn: $E = M/2$

Redn: $E = M/6$

$$\therefore EW_{H_3PO_3} = \frac{M}{2} + \frac{M}{6} = \frac{4M}{6}$$

$$E = \frac{2M}{3}$$

$$nf_{H_3PO_3} = 3/2$$

In addition to $-3, +3, +5$, 'P' exhibits +1 and +4 in its oxo cpds.

eg:— $\underset{+1}{H_3PO_2}$ & $H_4P_2O_6$ (Hypo phosphoric acid) ($O.S_P = +4$)

Note:— For As, Sb & Bi +3 stable w.r.t disproportionation

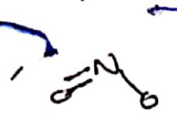
- [illegible]

Note:— 'N' exhibits $-\frac{1}{3}$ O.S in N_3H ($N_3H \longrightarrow$ Hydrazoic acid)

Anomolous behaviour of Nitrogen:- Due to its
- ① small size
- ② High E.N & I.E
- ③ Non-availability d-orbital

The propts are:- ① At room temp, N_2 is diatomic gas while others are solids

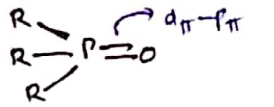
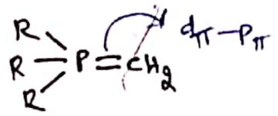
② 'N' has unique ability to form $P_\pi - P_\pi$ multiple bonds with itself and with others of small size & high E.N atoms (c, o etc)

eg:- $R-C\equiv N$,  , $ph-N=N-ph$, $N\equiv N$, $N\equiv O$ etc

'N' cannot form $P_\pi - d_\pi$ & $d_\pi - d_\pi$ bonds. ③ But heavier elements of this group not form $P_\pi - P_\pi$ bonds

Reason:- Atomic orbitals are large & diffuse that they cannot have effective overlapping.

∴ Heaviers (P, As etc) form $P_\pi - d_\pi$ and $d_\pi - d_\pi$ bonds.

eg①  eg②  $\ddot{P}(C_2H_5)_3$ & $\ddot{As}(C_6H_5)_3$

Act as ligands ($\bar{e}$ pair donars & forms $d_\pi - d_\pi$ bonds with Transition metals.

④ **Catenation:-** $P_4 > N_2$ (∵ catenation ∝ B.D.E)

Reason:- Bond strength :- P-P single bond (Strong bond) > $\ddot{N}-\ddot{N}$ single bond (Inter $\bar{e}$ nic rep^{n}s b/w Non-bonding $\bar{e}$s (L.P's) of 'N' atoms.

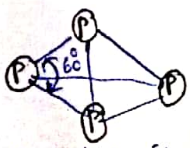
⑤ Eventhough 'N' exhibits +5 o.s, it can't form Pentahalide like NCl_5 but others form (PCl_5 & $AsCl_5$ etc)-

chemical propts :- Reactivity :- $P_4 > N_2$ ($N\equiv N$)

N_2 → chemically inert

Reason:- High B.D.E of $N\equiv N$ bond (941.4 kJ/mole)

Due to presence of angle strain, P_4 molecule is highly reactive than N_2.



IF P-P B.E = x what is the E req to to split 124g P_4? Ans:- 6x kJ)
(1 mole P_4 = 124g = contains 6 P-P bonds)

① Rn with H_2 (Formation of hydrides) :-

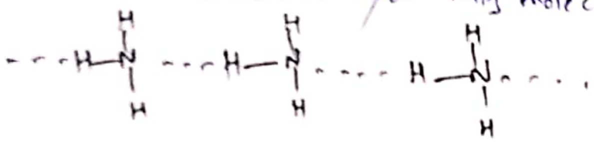
$$2E + 3H_2 \longrightarrow 2EH_3 \text{ (hydrides)}$$

(E = N, P, As, Sb, Bi)

(NH_3, PH_3, AsH_3, SbH_3, BiH_3)
Ammonia, Phosphine, Arsine, Stibine, Bismathine

At R.T, NH_3 is liquid

Reason :- presence of intermolecular H-bonds b/w NH_3 molecules

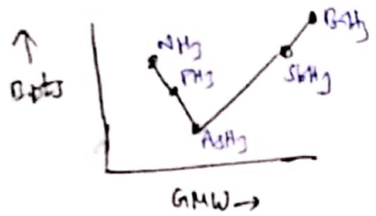


Foul smelling Gases ← At R.T (Covalent)

Reason :- Held by Vanderwall forces

Ⓐ M.pts :- $PH_3 < AsH_3 < SbH_3 < NH_3$

Ⓑ B.pts :- $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$



∴ B.pts ∝ Vanderwall forces (V.F ∝ GMW)

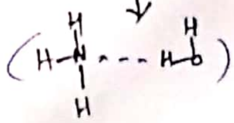
Note :- The abnormal high B.pt of NH_3 is due to H-bonds

③ Volatility order :- $PH_3 > AsH_3 > NH_3 > SbH_3 > BiH_3$ (Volatility $\propto \frac{1}{B.pts}$)

④ E-H Polarity ⑤ B.D.E (E-H bond) ⑥ Solubility in H_2O

⑦ Thermal stability ⑧ Basic nature ⑨ Bond angles

i.e 4, 5, 6, 7, 8, 9 ⟶ $:NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$



$H_3N: + \overset{\oplus}{H}OH \longrightarrow \overset{\oplus}{NH_4}$ (stable)

$H_3P: + \overset{\oplus}{H}OH \longrightarrow \overset{\oplus}{PH_4}$ (Unstable) Phosphonium Ion.

A :- BiH_3 is weak base i.e L.P less available for donation

R :- L.P on Bi spreads over large surface area

Bond angle :- $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
93.6^0, 91.8^0, 91.3^0

NH_3: N → sp^3, B.A = 107^0

B. Angles near to 90^0

Reason :- pure P-orbitals of P, As, Sb & Bi overlap with 1S orbitals of H-atoms along the axes.

✓ solubility of NH_3 in H_2O is due to form^n of H-bond with H_2O

Basic ⟶ $SbH_3 \geq BiH_3$

(1)

(10) E–H B.L. (Bond distance) (pm):– $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
(101.7 pm) (170.7 pm)

(11) <u>Standard enthalpy of formation (ΔH_f°)</u>:– NH_3 PH_3 AsH_3 SbH_3 BiH_3
$-46.1\ \frac{kJ}{mole}$ 13.4 66.4 145.1 278
(exo) endo

∴ Ease of formation:– $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
(forms easily and stable) (unstable)

(12) <u>Reducing power (R.P)</u>:– $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
(Good R.A)

$\left(R.P \propto \frac{1}{\text{stability}}\right)$

(13) <u>Rn with halogen</u>:– <u>(Form^n of halides)</u>:–

$E + X_2 \longrightarrow$ Halides ($\because E = N/P/As/Sb/Bi$)

① <u>Trihalides (EX_3)</u>

① covalent & stable
② BiF_3 is ionic
③ 'N' halides unstable but NF_3 stable

<u>stability</u>:– $NF_3 > NCl_3 > NBr_3$
(large difference in size)

(Add) <u>Lewis acid strength</u>:– $PCl_3 > AsCl_3 > SbCl_3$
(Small size 'P' receives $\bar{e}s$ easily)

$PF_3 > PCl_3 > PBr_3 > PI_3$

(Add) <u>Lewis Base strength</u>:– $NI_3 > NBr_3 > NCl_3 > NF_3$
(L.P less available on 'N' due to more EN 'F' atom)

(Add) B.A:– $PF_3 > PCl_3 > PBr_3 > PI_3$

② <u>Pentahalides (EX_5)</u>

① 'N' can't form NCl_5
<u>Reason</u>:– d-orbital not available

② P, As, Sb form. Because d-orbitals available
eg:– PCl_5

$P \longrightarrow 3s^2\ 3p^3\ 3d^0$

③ BiX_5 Pentahalides unstable
<u>Reason</u>:– Inert pair effect shown by $ns^2\ \bar{e}s$ in Bi

<u>Note</u>:– BiF_5 stable & ionic

<u>covalent</u>:– $EX_5 > EX_3$
(PCl_5) (PCl_3)

<u>Reason</u>:– Polarising power $\overset{+5}{P} > \overset{3+}{P}$

Rn with metals :- E + Metals ⟶ Binary ionic cpds ($O.S_E = -3$)

eg:- Ca_3N_2, Ca_3P_2, Na_3As, Zn_3Sb_2, Mg_3Bi_2

(Zinc stibinide) (Mg. Bismuthide)
(Zinc antimonide)

Rn with O_2 :- (Formation of oxides) :-

$$E + O_2 \longrightarrow \text{Oxides}$$

① Trioxides (E_2O_3)

N_2O_3 ⟶ Acidic
P_2O_3 (OR) P_4O_6 ⟶ Acidic
As_4O_6, Sb_4O_6 ⟶ Amphoteric
Bi_2O_3 ⟶ Basic

② Pentoxides (E_2O_5)

St. Acidic ⟵ N_2O_5
Acidic ⟵ P_2O_5 (OR) P_4O_{10}
W. Acidic ⟵ As_4O_{10}
Amphoteric ⟵ Sb_4O_{10}
W. Basic ⟵ Bi_2O_5

Note:- ① Trioxides & Pentoxides of P, As, Sb are dimers.

① Acidity of oxides ↓'ses from N → Bi
Reason :- '↑' sing the metallic character from N → Bi

② Acidity :- $E_2O_5 > E_2O_3$ (eg:- $N_2O_5 > N_2O_3$)
O.S N → +5 +3

Acidity :- $P_4O_{10} > P_4O_6$

Note:- $\boxed{\text{Acidic strength} \propto \text{O.No. element}}$

① $N_2O_3 + H_2O \longrightarrow 2HNO_2$ (Nitrous acid)

$$N_2O_3 \xleftarrow[-H_2O]{\Delta} \begin{matrix} HONO \\ HONO \end{matrix}$$

∴ N_2O_3 is anhydride of HNO_2

② $N_2O_5 + H_2O \longrightarrow 2HNO_3$

$$N_2O_5 \xleftarrow{-H_2O} \begin{matrix} HONO_2 \\ HONO_2 \end{matrix}$$

∴ N_2O_5 is anhydride of HNO_3 (Nitric acid)

③ $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$ (ortho P'rous acid)
$-H_2O$

④ $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$ (ortho P'ric acid)
$-H_2O$

∴ P_4O_6 & P_4O_{10} are anhydrides of H_3PO_3 & H_3PO_4 respectively

Note:- $E_2O_3 + H_2O \longrightarrow$ ous acids & $E_2O_5 + H_2O \longrightarrow$ ic acids

Dinitrogen: (N_2):-

① **From Air:-**

$$O_2 + N_2 \xrightarrow{\text{Liquified}} \underbrace{N_2 + O_2}_{} \text{ (Liquid mixture)}$$

(B.Pt N_2 = 77.2 K
B.Pt O_2 = 90 K)

$\downarrow$

N_2 collected 1st at 77.2 K & leaving the O_2 gas in vessel

② **Using aq. solⁿ of $NaNO_2$:- (Sodium nitrite):-**

$$NaNO_2 + NH_4Cl \longrightarrow N_2 + NaCl + 2H_2O + \text{small amts of impurities } (NO \ \& \ HNO_3)$$

NO $\downarrow$ Paramagnetic; HNO_3 $\downarrow$ O.A

N_2 $\downarrow$ Passed through aq. H_2SO_4 solution containing $K_2Cr_2O_7$ where NO & HNO_3 impurities are removed

③ **Thermal decompⁿ of $(NH_4)_2Cr_2O_7$:-**

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

$(2\overset{\oplus}{N}H_4 \ \ Cr_2O_7^{2-})$

N: $-3 \rightarrow 0$: $+3\times2 = (+6)$

Cr: $+6 \rightarrow +3$: $-3\times2 = (-6)$

GEW $(NH_4)_2Cr_2O_7 = \frac{M}{6}$

④ **Thermal decompⁿ of metal azides:-** very pure N_2 preparing

ⓐ $Ba(N_3)_2 \xrightarrow{\Delta} 3N_2 + Ba$ (V. pure)

ⓑ $2Na\overset{\ominus}{N_3} \xrightarrow{\Delta} 3N_2 + 2Na$ (V. pure)

Additional :- Prepⁿs :-

① $2NH_4IO_3 \xrightarrow{\Delta} N_2 + I_2 + O_2 + 4H_2O$ (Ammⁿ Iodate)

② $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ (Ammⁿ nitrite)

③ $2NH_3 + NaClO \longrightarrow N_2 + 3NaCl + 3H_2O$ (Sod. hypochlorite)

Physical propts:-

N_2:

- Low B.pt
- ① Low F.pt
- col-less, odourless, non-toxic and tasteless gas
- ④ ^{14}N & ^{15}N stable isotopes
- ⑤ low solubility in H_2O (At 273 K, 1 bar P, 23.2 c.c of N_2 dissolved in 1 litre of H_2O)

chemical propts :- ① chemically inert due to high B.D.E ($941.4\ kJ/mole$)

② Rcty ∝ Temp ③ **with metals :-** At high temp

$$N_2 + 3Mg \xrightarrow[\Delta]{\text{Directly}} Mg_3N_2$$

$$N_2 + Li \xrightarrow{\Delta} 2Li_3N \text{ (Ionic)}$$

④ **with O_2 :-**

$$N_2 + O_2 \underset{2000K}{\overset{\text{High T}}{\rightleftharpoons}} 2NO \ ; \ \Delta H = +180.8\ kJ$$

⑤ **with H_2 :-**

$$N_2 + 3H_2 \longrightarrow 2NH_3 \ ; \ \Delta H_r^\ominus = -92.2\ kJ$$

$$\therefore \Delta H_f^\ominus{}_{NH_3} = \frac{-92.2}{2} = -46.1\ kJ/mole$$

Uses of N_2 :- ① In the prepⁿ of NH_3

② As inert diluent for reactive chemicals

③ In the prepⁿ of industrial chemicals containing N_2

eg:- $CaC_2 + N_2 \longrightarrow \underbrace{CaCN_2 \text{ (OR) } (CaNCN) + C_{\text{Graphite}}}_{\text{Nitrolim}}$

Note:- $CaCN_2$ is calsium cyanamide

④ To provide inert atm in Iron (Fe) and steel industry

⑤ Liquid N_2 as refrigerent

⑥ To preserve biological materials, food items & in cryosurgery

AMMONIA :- (NH_3) :-

prepⁿ methods :

① **Decay of nitrogenous matter (Urea) :-** NH_3 is present in small amts in air & soil where it is formed by decay of nitrogenous matter

$$\underset{\text{(Urea)}}{NH_2-\overset{O}{\overset{\|}{C}}-NH_2} + 2H_2O \longrightarrow (NH_4)_2CO_3 \longrightarrow 2NH_3 + CO_2 + H_2O$$

② **From Ammonium salts :-** using NaOH (OR) $Ca(OH)_2$

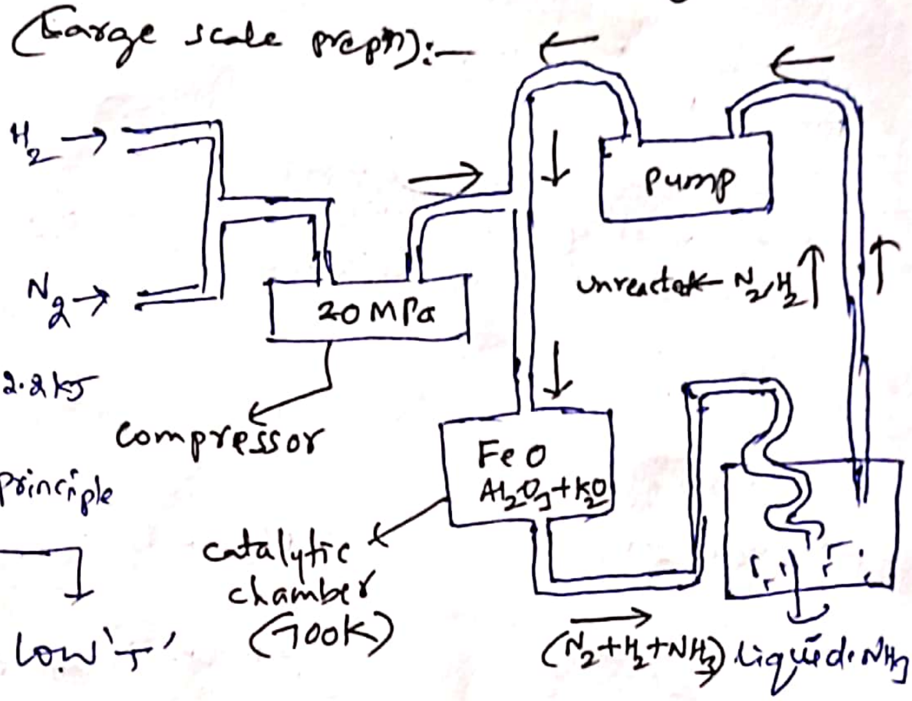
$$(NH_4)_2SO_4 + \underset{\text{(Caustic soda)}}{2NaOH} \xrightarrow{\Delta} 2NH_3\uparrow + Na_2SO_4 + H_2O$$

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} 2NH_3\uparrow + CaCl_2 + 2H_2O$$

$$NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3\uparrow + NaNO_3 + H_2O$$

Notes: NH_3 → ① Turns Red litmus Blue (Pungent smell) gas
→ ② Gives dense fumes (NH_4Cl) with glass rod dipped in con HCl

(3) Haber process :- (Large scale prepn):-



$N_2 + 3H_2 \rightleftharpoons 2NH_3;\ \Delta H_f^\circ = -92.2 kJ$

Acc. to Lechatelier's principle

(1) High 'P'

(2) Low 'T'

Needed to get more NH_3

$(1 atm = 10^5$ pascals$)$

1 Mega pascal $= 10^6$ pa

opt. conditions reqd :-

(1) opt. 'P' :- 20 MPa (OR) 200×10^5 pa (OR) 200 atm

(2) opt. 'T' :- 700 - 725 K

(3) present catalyst :- Iron oxide (FeO) (Earliear :- Iron (Fe))

(4) present promoter :- $K_2O + Al_2O_3$ (Earlier :- Mo)

$\therefore$ yield = 10 % (Less)

Drying of NH_3 :-

(1) CaO (quick lime) (Basic) using to dry NH_3

$NH_3 + CaO \longrightarrow$ No Rn
(Basic) (Basic)

(2) To dry NH_3 we should not use Con H_2SO_4, P_4O_{10} & Anhydr. $CaCl_2$

Reason :- Rn takes

$NH_3 + \underset{Con}{H_2SO_4} \longrightarrow (NH_4)_2SO_4$

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

$NH_3 + CaCl_2 \longrightarrow$ Addn cpd. $(CaCl_2 \cdot 8NH_3)$

Note :- NH_3 (OR) Amonium salts (NH_4Cl (OR) NH_4NO_3 etc) detected by Nessler's reagent (K_2HgI_4)

Phy. propts :-

NH_3:

① colorless & pungent odour gas

② 'N' sp^3 & Pyramidal


(Pyramidal)

③ Highly soluble in H_2O

Aq. soln is weak basic

($NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons \overset{\oplus}{NH_4} + \overset{\ominus}{OH}$)

(1000 volumes of NH_3 at 273K soluble in 1 volume of H_2O)

④ Like H_2O, NH_3 has inter molecular H-bonds in solid & liquid states.

∴ M.pt & B.pt abnormally High on the basis of GMW

chemical propts :-

① with Acids :-

① $NH_3 + HCl \longrightarrow NH_4Cl$

② $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

② Precipitation Rns :-

$$\underset{(aq)}{2NH_4OH} + \underset{(aq)}{ZnSO_4} \longrightarrow \underset{\text{wt ppt}}{Zn(OH)_2\downarrow} + (NH_4)_2SO_4$$

$$\underset{(aq)}{NH_4OH} + \underset{(aq)}{FeCl_3} \longrightarrow \underset{\substack{\text{Brown ppt} \\ \text{(Rust)}}}{Fe_2O_3\cdot xH_2O\downarrow} + NH_4Cl$$

③ Formn of complexes :- Acts ligand & forms complexes with transition metal ions. (Cu^{2+}, Ag^{+}, $Au^{\oplus}$, Zn^{2+} etc)

∴ NH_3 is used to detect Cu^{2+}, Ag^{+} etc ions in qualitative analysis.

(i) $$\underset{\substack{\text{Ligand} \\ \text{(Lewis Base)} \\ \bar{e}\text{ pair donar}}}{4NH_3} + \underset{(aq)}{Cu^{2+}} \rightleftharpoons \underset{(aq)}{[Cu(NH_3)_4]^{2+}}$$

Tetra amine copper(II) Ion, (H_2O soluble complex) Deep Blue.

(ii) $$\underset{\substack{(s) \\ \text{wt ppt}}}{AgCl} + \underset{(aq)}{2NH_3} \longrightarrow \underset{(aq)}{[Ag(NH_3)_2]Cl}$$ ($\because \overset{\oplus}{Ag}NO_3 + Na\overset{\ominus}{Cl} \rightarrow \underset{(s)}{AgCl}\downarrow + NaNO_3$)

Di ammine silver(I) Ion (H_2O soluble complex)

④ Rn with Cl_2 :-

$$NH_3 + \underset{(excess)}{3Cl_2} \longrightarrow NCl_3 + 3HCl$$

$$\underset{(excess)}{8NH_3} + \underset{(less)}{3Cl_2} \longrightarrow N_2 + 6NH_4Cl$$

Uses of NH_3 :- It is used

① As refrigerent (liq. NH_3)

② To detect Cu^{2+} & Ag^{+} ions in qualitative analysis

③ In manufacture of 'N' fertilisers like urea, NH_4NO_3 & $(NH_4)_2SO_4$ etc, $(NH_4)_3PO_4$

④ In manufacture of HNO_3 in ostwald method

(1) NH_3 prepⁿ by cyanamide process :- (Additional):-

(i) $CaC_2 + N_2 \xrightarrow{800-1100°C} CaCN_2 + C$ Graphite

($Ca=CN$)

Calsium. cyanamide

Nitrolim

(ii) $CaCN_2 + 3H_2O \longrightarrow 2NH_3\uparrow + CaCO_3$

Ammonia

(2) Hydrolysis of Trichlorides :- (Addistional):-

Easy of hydrolysis :- $NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$

$NCl_3 + 3H_2O \longrightarrow NH_3\uparrow + 3HOCl$ (Hypo chlorous acid)

$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$ (Ortho phosphorous acid)

$AsCl_3 + 3H_2O \longrightarrow H_3AsO_3 + 3HCl$ (Arsenious acid)

$SbCl_3 + 3H_2O \longrightarrow SbOCl\downarrow + 3HCl$

Antimony oxy chloride (Antimonyl ") wt ppt

$BiCl_3 + 3H_2O \longrightarrow BiOCl\downarrow + 2HCl$

Bismath oxy chloride (Bismathyl ") (wt ppt)

Oxides of Nitrogen :- N_2 combines with O_2 to form more no. of oxides, Because no. of unpaired $\bar{e}$s of both N & O are in same shell & they form multiple bonds easy.

Acidity oxides :- $N_2O < NO < N_2O_3 < NO_2 (N_2O_4) < N_2O_5$

$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

Nitrous acid (Nitric acid)

$2NO_2$ or N_2O_4 $\underset{-H_2O}{\overset{-H_2O}{\longleftarrow}}$ $HONO$, $HONO_2$

∴ NO_2 is mixed anhydride of HNO_2 & HNO_3

S.No.	'N' oxide	O.S 'N'	prep^n method	propts.
1	N_2O Dinitrogen oxide (OR) Nitrogen (I) oxide (OR) Nitrous oxide	+1	$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ Amm. nitrate ($\overset{\oplus}{NH_4}$ & $\overset{\ominus}{NO_3}$) O.S$_N = -3$ O.S$_N = +5$	① col. less gas ✓② Neutral ③ Diamagnetic
2.	NO Nitrogen monoxide (OR) Nitrogen (II) oxide	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow 2NO + Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O$	① col. less gas ② Neutral ③ Para
3	N_2O_3 Dinitrogen trioxide (OR) Nitrogen (III) oxide (Sesqui oxide)	+3	$2NO + N_2O_4$ (OR $2NO_2$) $\xrightarrow[\text{cooled}]{250K} 2N_2O_3$	① Blue solid ② W. Acidic ③ Anhydride of HNO_2

• sesqui oxide means when 3 atom of "O" attached with 2 atoms of other element. eg:- N_2O_3, Al_2O_3, La_2O_3 etc.

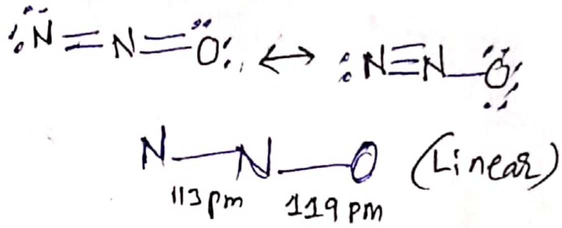
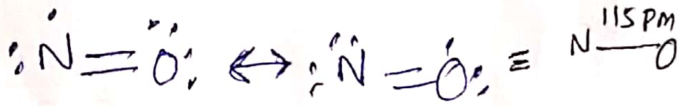
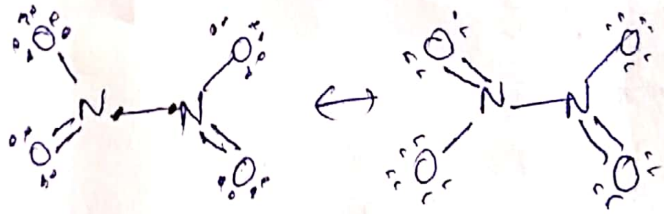
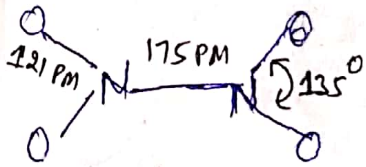
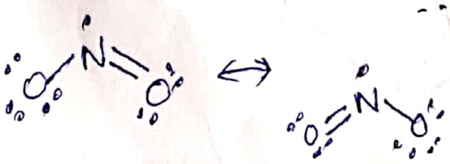
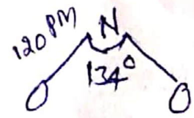
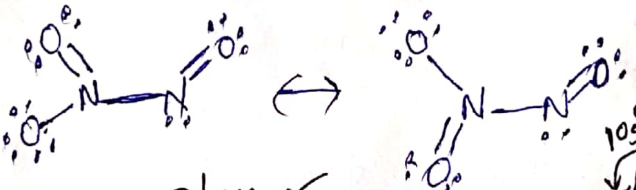
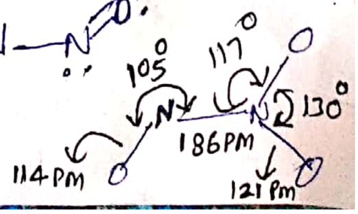
S.No.	'N' oxide	O.S 'N'	prep^n method	propts.
4	NO_2 Nitrogen dioxide (OR) Nitrogen (IV) oxide	+4	$Pb(NO_3)_2 \xrightarrow[673K]{\Delta} \underbrace{4NO_2\uparrow + O_2\uparrow}_{\text{para}} + 2PbO$; $M(NO_3)_2 \xrightarrow{\Delta} 4NO_2 + O_2 + 2MO$ (M = Be, Mg, Ca, Sr, Ba, Hg etc)	① Reddish brown gas ② Para ③ Acidic ④ mixed anhydride of HNO_2 & HNO_3
5	N_2O_4 Dinitrogen tetroxide (OR) Nitrogen (IV) oxide	+4	$2NO_2 \underset{\text{Heat}}{\overset{\text{Cool (-11°C) dimerisation}}{\rightleftharpoons}} N_2O_4$; NO_2: ① gas ② para ③ Reddish brown; N_2O_4: ① solid ② Dia ③ col. less	① col. less solid (OR) liquid ② Acidic
6	N_2O_5 Dinitrogen pentoxide (OR) Nitrogen (V) oxide	+5	$4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$	① col. less solid ② Acidic

Addi

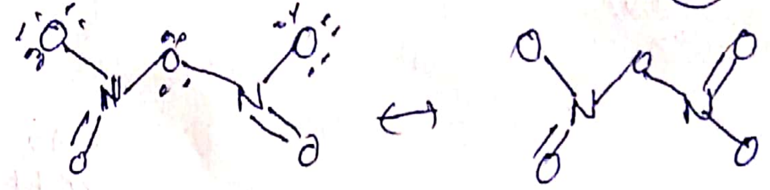
Note :- In solid & liquid states NO is diamagnetic due to demerisation.

$$\underset{\substack{(\text{odd})\\ \bar{e}s\\ \text{Para}}}{2NO} \longrightarrow \underset{\substack{(\text{Even } \bar{e}s)\\ \text{Dia}}}{N_2O_2}$$

∴ structures of 'N' oxides :-

S.No.	'N' oxide	structure
①	N_2O ① T. no. $\bar{e}s$ req = 24 ② $\bar{e}s$ available = 5×2+6 = 16 = 8 = T.p's to write lewis stru (outer most $\bar{e}s$) 8 $\bar{e}s$ = 4 = B.p's 4 = L.p's	
②	NO ① 2×8 = 16 $\bar{e}s$ ② 5+6 = 11 $\bar{e}s$ = 5 pairs + 1$\bar{e}$ 5 $\bar{e}s$ = 2 B.p's + 1$\bar{e}$ 3 = L.p's + 1$\bar{e}$	 ① Odd $\bar{e}$ molecule (bond) ② Para magnetic in gaseous state
③	N_2O_4 ① 6×8 = 48 $\bar{e}s$ ② 10+24 = 34 $\bar{e}s$ = 17 = T.p's 14 = 7 = B.p's 10 = L.p's	 (or)  ∴ planar (6 atoms in same plane)
④	NO_2 ① 3×8 = 24 $\bar{e}s$ 5+6×2 = 17 $\bar{e}s$ (8p + 1$\bar{e}$) 7 $\bar{e}s$ = 3 = B.P's + $\bar{e}$ LP = 5 & 1$\bar{e}$	  Angular
⑤	N_2O_3 ① 5×8 = 40 $\bar{e}s$ ② 10+18 = 28 = 14 = T.p's 12 = 6 = B.p's 8 = L.p's	 planar 

(6) N_2O_5

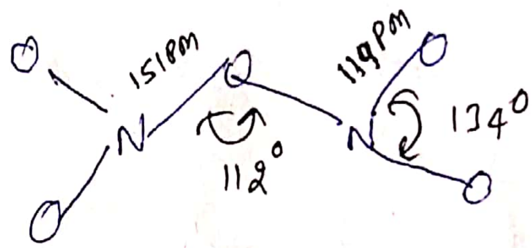


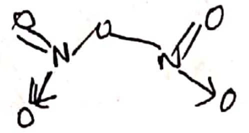
① $7 \times 8 = 56\bar{e}s$

② $10 + 30 = 40\bar{e}s = 20 = B.P's$

$\quad\quad 16 = 8 = B.P's$

$\quad\quad 12 = L.P's$





① 6 → Covalent

② 2 → Dative

③ No N–N bond

∴ planar

① $B.L_{N-N} \longrightarrow N_2O_3 > N_2O_4 > N_2O$

② $B.L_{N-O} \longrightarrow N_2O > NO$

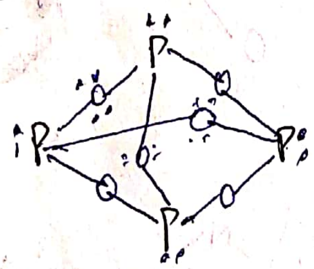
③ $B.A_{(ONO)} \longrightarrow N_2O_4 > NO_2 = N_2O_5 > N_2O_3$

$135° \quad 134° \quad 134° \quad 130°$

oxides of 'P' :

① P_4O_6 (P'rus trioxide)

structure :



① Each 'P' atom surrounded by 3 'O's

② T. L.P's = 16

③ P–O–P bonds = 6

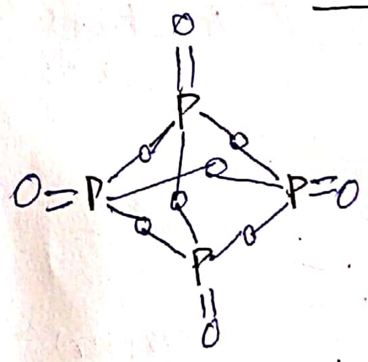
④ P–O bonds = 12

⑤ $C.V_P = 3$

⑥ No. Bridge 'O' atoms = 6

⑦ Anhydride of H_3PO_3

P_4O_{10} :- (P'rous pentoxide)



In this '4' $P\pi-d\pi$ bonds present

① 4 'O' atoms

② $10 \times 2 = 20$ (2 L.P's on each 'O' atom)

③ 6

④ P–O = 12 & P=O = 4

∴ Total = 16

⑤ $C.V_P = 5$

⑥ No. of bridge 'O's = 6

⑦ Anhydride of H_3PO_4

Oxo acids of 'N' :—

① $\overset{+1}{HNO}$ → Hyponitrous ($H_2N_2O_2$) → HO—N=N—OH

② $\overset{+3}{HNO_2}$ → Nitrous → HO—N=O

③ $\overset{+5}{HNO_3}$ → Nitric → HO—N(=O)=O

④ $\overset{+5}{HNO_4}$ → Per nitric acid → O=N(=O)—O—OH

① Nitric Acid (HNO_3) :—

Preph methods :—

① Lab. method :— From nitrate salts

(i) $\underset{(aq)}{NaNO_3} + \underset{conc}{H_2SO_4} \xrightarrow{\text{in glass retort}} HNO_3 + NaHSO_4$

(ii) $KNO_3 + \underset{conc}{H_2SO_4} \longrightarrow HNO_3 + KHSO_4$

② Ostwald method :— (on large scale) :— Depends on the catalytic oxdn of NH_3 by atm O_2

① $4\overset{-3}{N}H_3 + 5\underset{(Air)}{\overset{0}{O_2}} \xrightarrow[\substack{500K \text{ 'T'} \\ 9 \text{ bar 'p'}}]{\text{Pt \& Rh gauge}} 4\overset{+2}{N}\overset{-2}{O} + 6H_2O + \text{Heat (exo)}$

$(+5) \times 4 = (+20)$ oxdn

$-2\times2 = (-4) \times 5 = (-20)$ Redn

NO unstable at high 'T'

② $\underset{(g)}{2NO} + \underset{(g)}{O_2} \longrightarrow \underset{(g)}{2NO_2}$

③ $\underset{(g)}{3NO_2} + \underset{(l)}{H_2O} \longrightarrow \underset{(aq)}{2HNO_3} + \underset{(g)}{NO}$ Recycled again to get HNO_3

↓ distillation & concentrated

68% HNO_3 by mass $\xrightarrow[\text{Con } H_2SO_4]{\text{Dehydration with}}$ 98% HNO_3

Q How many moles O_2 reqd to oxidise 1 mole NH_3 into NO (Ans. $\frac{5}{4}$)

$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$ (4 mol NH_3 ⟶ 5 mol O_2
1 mol NH_3 ⟶)

Phy. propts :—

HNO_3

① colless liquid

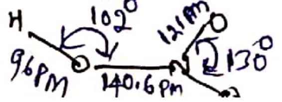
② M.Pt = 231.4K

③ B.Pt = 355.6K

④ Lab HNO_3 = 68% by mass

⑤ Str. acidic in aq. soln
$\underset{A\text{I}}{HNO_3} + \underset{B\text{II}}{H_2O} \rightleftharpoons \underset{A\text{II}}{H_3O^{\oplus}} + \underset{B\text{I}}{NO_3^{\ominus}}$

⑥ Planar in gaseous state



Note:- HNO_3 acquires yellow colour due to decompⁿ by sunlight into NO_2

$$4HNO_3 \xrightarrow{h\nu} 4NO_2 + 2H_2O + O_2 \text{ (Additional)}$$

che. propts :-

Oxidising propts of HNO_3 :- It acts as strong oxidising agent (O.A)

(A) with metals :- (Cu, Zn) :- HNO_3 attacks most metals except noble metals like Pt & Au.

$$HNO_3 + \text{Metals} \longrightarrow \text{M-nitrate} + 2(H)$$

(Nascent hydrogen)

Nascent hydrogen reduces HNO_3 to → N_2O, → NO, → NO_2

The prodts depend on the → ① conⁿ of HNO_3 → ② Nature of metal → ③ temperature (T)

using conc HNO_3 :- con HNO_3 oxidises Cu & Zn to $Cu(NO_3)_2$ and $Zn(NO_3)_2$ & it is reduced to NO_2 gas

$$\underset{(conc)}{4HNO_3} + 1Zn \longrightarrow Zn(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

$$\underset{conc}{4H\overset{+5}{N}O_3} + 1\overset{0}{Cu} \longrightarrow \overset{+2}{Cu}(NO_3)_2 + 2\overset{+4}{N}O_2\uparrow + 2H_2O$$

(+2) × 1

(−1) × 2

Note:- Not only Zn, Cu also taking with Ag, Pb, Hg NO_2 liberated

$$2HNO_3 + 1Cu \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

∴ 2mole HNO_3 ≡ 1 mole Zn (64g) (OR) = 1 mole Cu (63.5g)

(1 G.Atom Zn) (OR) (1 G.Atom Cu)

using Dil HNO_3 :-

(i) $$\underset{(Dil)}{8H\overset{+5}{N}O_3} + 3\overset{0}{Cu} \longrightarrow 3\overset{+2}{Cu}(NO_3)_2 + 2\overset{+2}{N}O + 4H_2O$$

(+2) × 3 oxdⁿ

(−3) Redⁿ × 2

∴ 2 moles HNO_3 oxidises 3 mole Cu (OR) 3 G.atoms Cu (OR) 3×63.5g Cu

(ii) $$\underset{(Dil)}{10H\overset{+5}{N}O_3} + 4\overset{0}{Zn} \longrightarrow 4\overset{+2}{Zn}(NO_3)_2 + \overset{+1}{N_2}O + 5H_2O$$

(Fe, Sn)

(+2) × 4

(−4) × 2

∴ 2mole HNO_3 oxidises 4 mole Zn (OR) 4 G.Atoms Zn (OR) 4×64g Zn

1. How many G.atoms Cu oxidised by 1 mole dil HNO_3. (Ans:- 1.5 g.atom Cu)

Soln:- $2\overset{+5}{HNO_3}_{(dil)} + 3\overset{0}{Cu} \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+2}{NO} + H_2O$

$(+2 \times 3)$, $(-3) \times 2$

2 mole dil HNO_3 — 3 mole Cu / 3 G.Atom Cu

1 mole — ?

$\frac{1 \times 3 \text{ G.atom}}{2}$

$= \frac{3}{2} = 1.5$ G-atom

2. How many grams of Cu oxidised by 1 mole dil HNO_3?

2 mole HNO_3 ——— 3×63.5 g Cu

1 mole HNO_3 ——— ?

$\frac{1 \times 3 \times 63.5}{2}$ $= 1.5 \times 63.5$ g Cu

Note:- Cr, Fe, Ni & Al metals are insoluble in Conc. HNO_3. This is due to formation of passive ~~film~~ film of oxide on their surface

Rn with Non-metals:- Conc HNO_3 oxidises non-metals like
- (1) $C \rightarrow CO_2$
- (2) $I_2 \rightarrow HIO_3$
- (3) $P_4 \rightarrow H_3PO_4$
- (4) $S_8 \rightarrow H_2SO_4$

Reduced to NO_2 gas

(i) $4\overset{+5}{HNO_3}_{(Conc)} + 1\overset{0}{C} \longrightarrow \overset{+4}{CO_2}\uparrow + 4\overset{+4}{NO_2}\uparrow + 2H_2O$

$(+4) \times 1$, $(-1) \times 4$

$\therefore$ 4 mole HNO_3 oxidises 1 mole 'c'

(ii) $10\overset{+5}{HNO_3}_{(Conc)} + 1\overset{0}{I_2} \longrightarrow 2\overset{+5}{HIO_3} + 10\overset{+4}{NO_2} + 4H_2O$

Iodic acid

$+5 \times 2 = +10 \times 1$, $(-1) \times 10$

$\therefore EW_{I_2} = \frac{M}{2} = \frac{254}{2}$

$\therefore$ 10 moles HNO_3 oxidises 1 mole I_2

(iii) $20\overset{+5}{HNO_3} + 1\overset{0}{P_4} \longrightarrow 4H_3\overset{+5}{PO_4} + 20\overset{+4}{NO_2}\uparrow + 4H_2O$

ortho phosphoric acid

$+5 \times 4 = +20 \times 1$, $(-1) \times 20$

$EW_{P_4} = \frac{M}{20} = \frac{31 \times 4}{20}$

(iv) $48\overset{+5}{HNO_3} + 1\overset{0}{S_8} \longrightarrow 8H_2\overset{+6}{SO_4} + 48\overset{+4}{NO_2}\uparrow + 16H_2O$

$+6 \times 8 = +48 \times 1$, $(-1) \times 48$

$\therefore EW_{S_8} = \frac{M}{48} = \frac{256}{48}$

Additional:- Very dil HNO_3 oxidises Zn to $Zn(NO_3)_2$

$4Zn + 10HNO_{3\,(Very\ dil)} \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

$\therefore 4\overset{0}{Zn} + 1NO_3^{\ominus} \longrightarrow \overset{2+}{Zn} + \overset{\oplus}{NH_4}$

260g Zn = 4 mole Zn = 1 mole HNO_3

(OR)

$\overset{0}{Zn} + \overset{+5}{NO_3^{\ominus}} \longrightarrow \overset{2+}{Zn} + \overset{\oplus}{NH_4}$

Brown ring Test :-

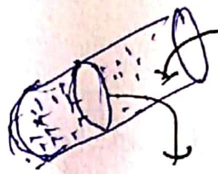
It is used to confirm the nitrate ($NO_3^{\ominus}$) ion in inorganic qualitative analysis, This depends on the ability of Fe^{2+} to reduce $NO_3^{\ominus}$ to NO.

It is given by nitrate salts → NH_4NO_3, $Pb(NO_3)_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Ba(NO_3)_2$ etc.

Add freshly prepd $FeSO_4$

Aq. soln of nitrate salt

Test tube



Con H_2SO_4 adding drop by drop

Brown ring formed at the junction of solution & H_2SO_4 layer.

Note :- Brown ring formn indicates the presence of $NO_3^{\ominus}$ ion

$$\underset{(O.A)}{NO_3^{\ominus}} + \underset{(R.A)}{3Fe^{2+}} + H^{\oplus} \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$$

($\because Fe^{2+} + 6H_2O \rightarrow [Fe(H_2O)_6]^{2+}$)
Hexa aqua Iron (II) Ion

Brown ring complex
Penta aqua nitrosonium Iron (I) Ion

$O.S_{Fe} = +1$

($\because [Fe(H_2O)_5(NO)]^{2+}$, $NO^{\oplus}$)

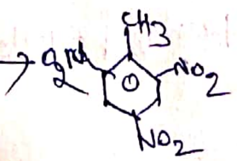
$x + 0 + 1 = +2$

$x = +1$

Uses of HNO_3 :-

HNO_3:

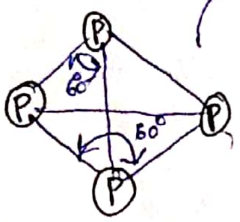
1. In manufacture of fertilisers like NH_4NO_3
2. In prepn of explosives
   Eg. (1) Nitroglecerine
   (2) T.N.T →



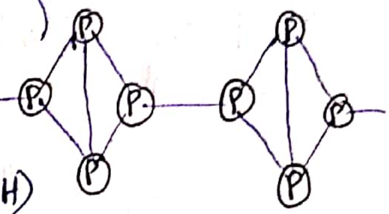
   2,4,6-trinitro Tolune
3. In pyrotechnics
4. pickling of stainless steel
5. For etching of metals
6. As oxidiser in Rocket fuel
7. For the prepn of Aquaregia
   Con HNO_3 + Con HCl (1:3)

Allotropes of Phosphorous (P_4):–
- ① wt
- ② Red
- ③ Black

Reactivity:– wt P_4 > Red P_4



$$\underset{\text{(white)}}{P_4} \xrightarrow[\text{Inert atm, heated few days}]{573K} \underset{\text{(Red) (Polymeric T.H)}}{(P_4)_n}$$



(T.H units joined by P-P bonds)

① $C.V_P = 3$
② $O.N_P = 0$
③ $P\hat{P}P = 60^\circ$
④ No. P-P bonds = 6

P_4 (white) → ① 473K ② High P' → **β – Black P_4**
(① Not burn in air upto 673 K)
② Non-metallic conductor like graphite

$(P_4)_n$ (Red) → ① 803K in sealed tube → **α – Black P_4**
(① sublimed in air)
② opaque monoclinic or Rhombohedral
③ Not oxidise in air

wt P_4
① consists of discrete P_4 molecules held together by Vanderwaal forces
② Insoluble in H_2O
③ soluble in CS_2
④ poisonous
⑤ Glow in dark (chemiluminescence)
⑥ Translucent white waxy solid
⑦ A:– Highly reactive & unstable
R:– presence of strain i.e angle strain

⑧ wt P_4 catches fire in air to give P_4O_{10} white fumes. Therefore it is stored in H_2O because of its ignition temparature.

$$P_4 + 5O_2 \longrightarrow P_4O_{10} \text{ white fumes}$$

⑨ wt P_4 dissolves in boiling NaOH solution in an inert atm to give Phosphine (PH_3).

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{sod. hypo phosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3}$$

Red P_4

- (1) P_4O_{10} white fumes (O_2)
- (2) Insoluble in both H_2O and CS_2
- (3) It is Non-poisonous
- (4) Not glow in dark
- (5) Iron grey lustre
- (6) $\xrightarrow{\Delta}$ α-Black P_4
- (7) Much less reactive than wt P_4
- (8) odourless solid

Phosphine (PH_3) :–

Prepn :– (1) From Metal phosphides (Ca_3P_2, Na_3P) :– By hydrolysis (or) using acid

(i) $Ca_3P_2 + 6H_2O \longrightarrow 2PH_3\uparrow + 3Ca(OH)_2$ (or) $Ca_3P_2 + 6HCl \longrightarrow 2PH_3\uparrow + 3CaCl_2$

(ii) $Na_3P + 3HCl \longrightarrow PH_3\uparrow + 3NaCl$

(2) Lab method :– (From wt P_4) :–

$$P_4 + 3NaOH + 3H_2O \xrightarrow[\text{Coal gas}]{\text{Inert atm of } CO_2 \text{ (OR)}} \underset{\text{Phosphine}}{PH_3\uparrow} + \underset{\text{sod. hypophosphite}}{3NaH_2PO_2}$$

(Coal gas used to remove air)

Phosphine: It is non-inflammable in pure state

PH_3 is inflammable in presence of P_2H_4 (Diphosphine) & P_4 Vapours as impurities. To remove these impurities, PH_3 is absorbed into HI where it forms PH_4I.

$$\underset{\text{(Base)}}{PH_3} + \underset{\text{(Acid)}}{HI} \longrightarrow \underset{\text{Phoshonium Iodide}}{PH_4I}$$

PH_4I on treatment with KOH to give PH_3

$$PH_4I + KOH \longrightarrow \underset{\text{(Pure)}}{PH_3\uparrow} + KI + H_2O$$

Physical propts :–

PH_3

- (1) colourless gas
- (2) slightly soluble in H_2O
- (3) Highly poisonous
- (4) Rotten fishy smell
- (5) Explodes in contact with traces of oxidising Agents like (a) HNO_3 (b) Cl_2 (c) Br_2 vapours

Che. Props of PH_3:-

(1) Decomposition:-

$$4PH_3 \text{ (aq)} \xrightarrow{\text{Sunlight}} (P_4)_n + 6H_2$$

Red P_4

(2) Rn with $CuSO_4$ & $HgCl_2$:- (Absorption of PH_3):-

$$2PH_3 + 3CuSO_4 \text{ (aq)} \xrightarrow{\text{Absorption}} Cu_3P_2 \downarrow + 3H_2SO_4$$

cupric phosphide (Black ppt)

$$2PH_3 + 3HgCl_2 \text{ (aq)} \xrightarrow{\text{Absorption}} Hg_3P_2 \downarrow + 6HCl$$

Mercuric phosphide

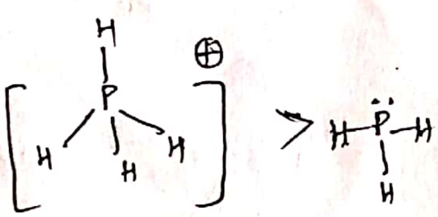
(3) **Basic nature**:- PH_3 behaves as weak base & hence it forms salts with HBr and HI acids

$$\underset{\substack{\text{(W.B)} \\ \text{(Lewis base)}}}{PH_3} + \underset{\text{(acid)}}{HBr} \longrightarrow \underset{\text{(Phosphonium bromide)}}{PH_4Br}$$

&

$$\underset{\text{(W.B)}}{PH_3} + \underset{\text{(acid)}}{HI} \longrightarrow \underset{\text{Phosphonium Iodide}}{PH_4I}$$

Bond angle:- $\overset{\oplus}{PH_4} > PH_3$ i.e



B.A° ~ 109° (No LP on 'P' atom)

B.A = 93° (L.P–B.P rep^n greater than B.P–B.P)

Uses:- PH_3 used

1. In making smoke screens
2. The spontaneous comb^n of PH_3 is technically used in **Holme's signals** (contain CaC_2 + Ca_3P_2)

(calsium carbide) (calsium phosphide)

Are pierced & thrown in the sea when gases evolved burn & serve as a signal.

'P' halides:-
- (1) PX_3 ($X = F, Cl, Br, I$)
- (2) PX_5 ($X = F, Cl, Br$), But PI_5 unstable due to large size of 'I' atom

① PCl_3 (Phosphorous trichloride) :–

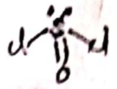
prepⁿ methods :– ① Passing dry Cl_2 gas over hot wt P_4

$$\underset{\text{(Hot wt)}}{P_4} + \underset{\text{(limited)}}{6Cl_2} \xrightarrow{\Delta} 4PCl_3$$

② using wt P_4 & $SOCl_2$:– $P_4 + 8\,\underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow PCl_3 + 2S_2Cl_2 + 4SO_2\uparrow$

S_2Cl_2 → (Sulphur mono chloride)

SO_2 → (Angular) ① $S \to sp^2$



① 's' → sp^3
② Trigonal Pyramidal

Propts :– ① It is colourless oily liquid & chlorinating Reagent

② **Hydrolysis** :– $PCl_3 + \underset{\text{(moist air)}}{3H_2O} \longrightarrow H_3PO_3 + 3HCl$

ortho phosphorous acid (Phophonic acid) (wt fumes)

③ **Rⁿ with organic cpds** :–

$PCl_3 + 3CH_3-\overset{O}{\overset{\|}{C}}-OH \longrightarrow 3CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$

Acetic acid (Ethanoic acid) → Acetyl chloride

$PCl_3 + CH_3-CH_2-OH \longrightarrow 3CH_3-CH_2-Cl + H_3PO_3$

Ethanol → Ethyl chloride

Addimal – PCl_3 is R.A & it reduces SO_3 to SO_2

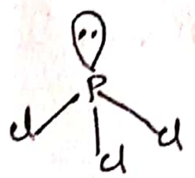
$$PCl_3 + \overset{+6}{SO_3} \xrightarrow{\text{Redⁿ}} \overset{+4}{SO_2} + POCl_3$$

(Phosphoryl chloride)

structure :– $P \to sp^3$

$P \to [Ne]\ 3s^2\ 3p^3$

Pyramidal



Repulsion → L.P–B.P > B.P–B.P

Uses :– PCl_3 used in the prepⁿ of C_2H_5Cl & CH_3COCl

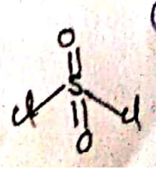
–: (PCl_5) :– Phosphorous penta chloride

prepⁿ methods :–

① $\underset{\text{(wt)}}{P_4} + \underset{\text{(excess)}}{10Cl_2} \longrightarrow 4PCl_5$

② $\underset{\text{(wt)}}{P_4} + 10\,\underset{\text{(sulphuryl chloride)}}{SO_2Cl_2} \longrightarrow 4PCl_5 + 10SO_2\uparrow$

$S \to sp^3$
T.H



① $S \to sp^2$
② geo → Angular

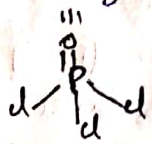
Props of PCl_5 :— ① It is pale Yellow solid (wt powder)

② $\underset{(S)}{PCl_5} \xrightarrow[\text{Sublimation up to } 160^\circ C]{\Delta} \underset{(g)}{PCl_5} \xrightarrow[\text{Decompn } (\Delta)]{\text{st. heating}} PCl_3 + Cl_2$

③ **Rn with organic cpds :—** (CH_3CH_2OH & CH_3COOH)

$PCl_5 + CH_3CH_2OH \longrightarrow \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + POCl_3 + HCl$

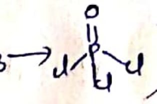
$PCl_5 + CH_3COOH \longrightarrow \underset{\text{Acetylchloride}}{CH_3COCl} + POCl_3 + HCl$



($P \to sp^3$ & T.H)

④ **Hydrolysis :—** undergo hydrolysis in moist air 1st gives $POCl_3$ & HCl & finally gives H_3PO_4

$PCl_5 + H_2O \xrightarrow{\text{Partial hydrolysis}} POCl_3 + 2HCl$ — ①

($\because POCl_3 \to$ )

$P \to sp^3$, T.H

$POCl_3 + 3H_2O \xrightarrow{\text{complete hydrn.}} H_3PO_4 + 3HCl$ — ②

Note :— with excess of H_2O, $PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$

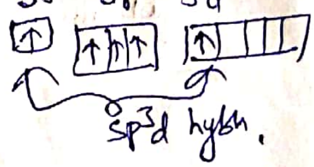
⑤ **Rn with metals :—** (Ag & Sn) :—

$PCl_5 + 2Ag \longrightarrow 2AgCl + PCl_3$

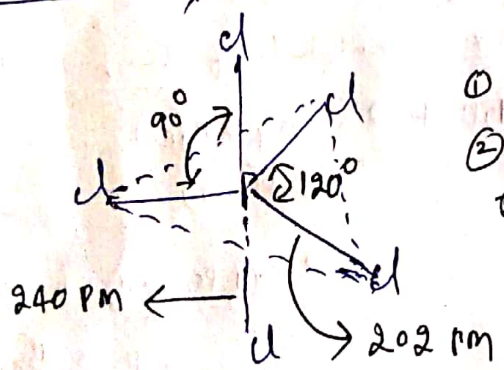
$2PCl_5 + Sn \longrightarrow SnCl_4 + 2PCl_3$

str. of PCl_5 :— P-atom is sp^3d hybridised

$P \to$ Ex. config $\to 3s^1\ 3p^3\ 3d^1$



sp³d hybn.



① Trigonal Bipyramidal

② No. 90° angles = 6

③ No. 120° " = 3

④ No. 180° = 1

⑤ T-No. atoms in same plane = 4

⑥ Axial P-Cl B.L = 240 PM

⑦ Equ P-Cl B.L = 202 PM

Note : ① In PCl_5 all bonds are not ~~equal~~ equivalent

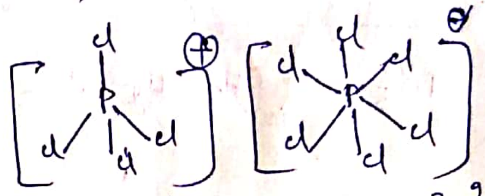
② R:— In PCl_5 axial P-Cl bonds are longer and weaker to equatorial bonds & therefore axial B.P's suffer more repulsions to equatorial B.P's

A:— PCl_5 is higly reactive and unstable

Ans:— both A & R true & 'R' is explanation of 'A'

In solid state PCl_5 exists as ionic solid which consists of $[PCl_4]^{\oplus}$ & $[PCl_6]^{\ominus}$ ions.

$$\underset{(s)}{2PCl_5} \longrightarrow \underset{\text{Cation}}{[PCl_4]^{+}} \; \underset{\text{Anion}}{[PCl_6]^{\ominus}}$$



$P \rightarrow sp^3$ T.H $\qquad$ $P \rightarrow sp^3d^2$ O.H

Note:-

$\underset{(s)}{PBr_5} \rightleftharpoons [PBr_4]^{\oplus} Br^{\ominus}$. Here the anion $[PBr_6]^{\ominus}$ is not possible, Because large size of 'Br' atom.

Q:- NF_3 not hydrolyse but NCl_3 hydrolyse.

Reason:- In NF_3 neither 'N' nor 'F' can accomodate a LP of e's of H_2O due to absence of vacant d-orbitals in 'N' OR 'F' where as in NCl_3, 'Cl' has vacant d-orbitals & receives LP e's from H_2O.

$$NCl_3 + H\text{-}O\text{-}H \xrightarrow[-HOCl]{} Cl_2NH \xrightarrow[-HOCl]{H-O-H} ClNH_2 \xrightarrow[-HOCl]{H-O-H} \underset{\text{Ammonia}}{NH_3}$$

OR

$$NCl_3 + 3H_2O \longrightarrow \underset{\text{Ammonia}}{NH_3} + 3HOCl$$

Note:- PF_3 and PF_5 are not hydrolyse

Reason:- P-F bond is stronger than P-O covalent bond

Calsium super phosphate:- OR **super phosphate of lime** (Additional)

$$(\underset{\text{Cal-H-Phosphate}}{Ca(H_2PO_4)_2 \cdot H_2O} + \underset{\text{(gypsum)}}{2\,CaSO_4 \cdot 2H_2O})$$

Prepn:-

$$\underset{\text{(Insoluble in } H_2O)}{Ca_3(PO_4)_2} + \underset{\substack{\text{Conc}\\(70\%)}}{H_2SO_4} + 5H_2O \longrightarrow \underset{\text{S.P. of lime}}{Ca(H_2PO_4)_2 \cdot H_2O + 2\,CaSO_4 \cdot 2H_2O}$$

$Ca_3(PO_4)_2$ ↓ present in (Bone ash OR phosphorite powder)

S.P. of lime ↓ (16—20% P_2O_5)

Triple phosphate of Lime:- $Ca(H_2PO_4)_2$

Prepn:-

$$Ca_3(PO_4)_2 + \underset{(70\%)}{4\,H_3PO_4} \longrightarrow 3\,Ca(H_2PO_4)_2$$

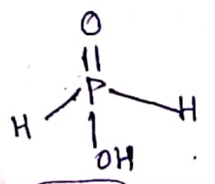
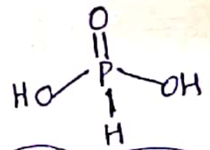
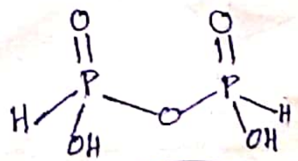
① Not contain $CaSO_4$
② 42—46% P_2O_5 i.e P_2O_5 in this 3 times of Cal-super-phosphate.

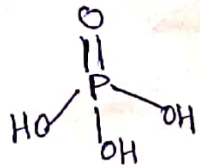
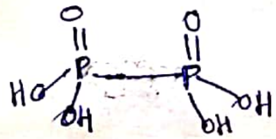
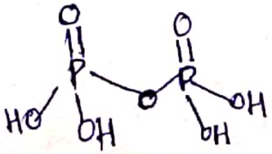
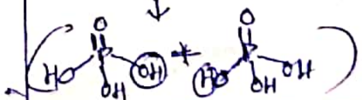
Solubility in H_2O:- T.P. Lime > Sup. Pho. lime

OXO ACIDS of 'P'

- ① -ous type :— H_3PO_2, H_3PO_3 and $H_4P_2O_5$
- ② -ic type :— H_3PO_4, $H_4P_2O_6$ $H_4P_2O_7$ and $(HPO_3)_n$

The compositions of oxo acids are inter related in terms of loss or gain of H_2O or 'O' atom.

S.No.	Formula	Name	O.S 'P'	Structure	Information	Reactants reqd for prepn
1.	H_3PO_2 $P \rightarrow sp^3$	Hypo-phosphorous acid or phosphinic acid	+1	 Basicity = 1 $H_3PO_2 + NaOH \rightarrow NaH_2PO_2 + H_2O$ (sodi. hypo phosphite) Neutral salt	1 P=O bond 2 P–H bonds 1 P–OH bond 1 $p\pi-d\pi$ bond	P_4 (wt) + NaOH (alkali) or $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$ $H_3PO_2 \leftarrow HCl\ (-NaCl)$
2.	H_3PO_3 $P \rightarrow sp^3$	ortho phosphorous acid or phosphonic acid	+3	 Basicity = 2 $H_3PO_3 \xrightarrow[-H_2O]{NaOH} NaH_2PO_3 \xrightarrow[-H_2O]{NaOH} Na_2HPO_3$ sodium dihydrogen phosphite; Disodium-H-phosphite	1 P=O bond 2 P–OH bonds 1 P–H bond 1 $p\pi-d\pi$ bond	$PCl_3 + H_2O$ or $P_4O_6 + H_2O$
3.	$H_4P_2O_5$ $P \rightarrow sp^3$ $+4+2x-10=0$	Pyro phosphorous acid	+3	 Basicity = 2 10 σ & 2 'π' bonds	2 P=O bonds 2 P–H bonds 2 P–OH bonds 1 P–O–P bond	$H_3PO_3 + PCl_3$

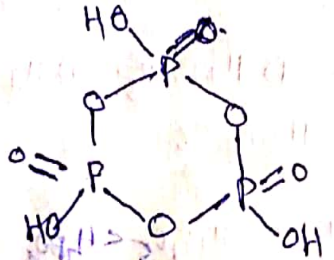
S.No	Formula	Name	O.S 'P'	Structure	Information	Reactants req^d for prep^n
4	H_3PO_4 $P \rightarrow sp^3$	ortho phosphoric acid	+5	 Basicity = 3	1 P=O bond 3 P–OH bonds	P_4O_{10} & H_2O OR PCl_5 & H_2O
		$H_3PO_4 \xrightarrow[-H_2O]{NaOH}$	NaH_2PO_4 (Acidic salt) sodium ~~H~~ phosphate	$\xrightarrow[-H_2O]{NaOH}$	$Na_2HPO_4 \xrightarrow[-H_2O]{NaOH}$ (Acidic salt) Disodium ~~H~~ phosphate	Na_3PO_4 (Neutral salt) Sodium phosphate
5.	$H_4P_2O_6$ $P \rightarrow sp^3$	Hypophosphoric acid (11σ & 2π)	+4	 Basicity = 4	2 P=O bonds 4 P–OH bonds 1 P–P bond 2 $p\pi$–$d\pi$ bonds	Red P_4 + NaOH
6.	$H_4P_2O_7$ $P \rightarrow sp^3$	Pyrophosphoric acid (12σ & 2π)	+5	 Basicity = 4	2 P=O bonds 1 P–O–P bond 4 P–OH bonds 2 $p\pi$–$d\pi$ bonds	Heating the H_3PO_4 $2H_3PO_4 \xrightarrow[-H_2O]{\Delta\ 520K} H_4P_2O_7$ 
7.	$(HPO_3)_n$	Poly metaphosphoric acid	-	–	–	H_3PO_3 and Br_2 ($H_3PO_3 + Br_2 \xrightarrow{\Delta} HPO_3 + 2HBr$)

HPO_3 ← meta phosphoric acid

① $(HPO_3)_3$ OR $H_3P_3O_9$

(cyclo trimetaphosphoric acid)

|||



① $P \rightarrow sp^3$ ② '3' P=O bonds

③ '3' P-OH bonds

④ '3' P-O-P bonds

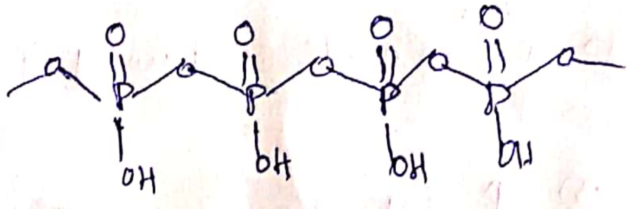
⑤ '6' P-O bonds

⑥ Each 'P' atom surrounded by 4 'O' atoms

⑦ $C.V_p = 5$

$(HPO_3)_n$

(Poly metaphosphoric acid)



① $P \rightarrow sp^3$

② $C.V_p = 5$

③ Each 'P' atom surrounded by 4 'O' atoms.

① All oxo acids contain atleast 1 P=O bond & 1 P-OH bond

(2) → Oxo acid ←

① In which 'P' O.S is less than +5 contain either P-H (H_3PO_2, $H_4P_2O_5$) OR P-P bonds ($H_4P_2O_6$) but not both

② In which $O.S_P = +3$ undergo disproportionation to lower & higher oxidation states.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

∴ H_3PO_3 acts as strong R.A & weak O.A

③ Ic acids not contain P-H bonds
eg:- $(HPO_3)_n$, H_3PO_4, $H_4P_2O_7$, $H_4P_2O_6$

③ 'P' oxo acids containing P-H bonds are good Reducing agents

∴ Reducing power (R.P) ∝ No. P-H bonds

$\therefore$ R.P $\longrightarrow H_3PO_2 > H_3PO_3 > H_3PO_4$
(Good R.A) (O.A)

H_3PO_2 reduces $\longrightarrow$
- $AgNO_3 \rightarrow Ag$ ✓
- $AuNO_3 \rightarrow Au$
- $HgCl_2 \rightarrow Hg$

(Au, Hg) $\rightarrow$ Additional.

$$\overset{+1}{H_3PO_2}\,(R.A) + 4\overset{+1}{Ag}NO_3 + 2H_2O \longrightarrow 4\overset{0}{Ag} + H_3\overset{+5}{P}O_4 + 4HNO_3$$

Redn (−1) × 4

oxdn (+4) × 1

$\therefore EW_{H_3PO_2} = M/4$

① 'P' oxo acids containing P–O–P bonds are ① $H_4P_2O_5$ ② $H_4P_2O_7$

② 'P' " " " " P–P bond is $H_4P_2O_6$

③ ↑'ing the no. of P–OH bonds $\longrightarrow H_3PO_2 < H_3PO_3 = H_4P_2O_5 < H_3PO_4 \equiv (HPO_3)_3$
$< H_4P_2O_6 \equiv H_4P_2O_7$

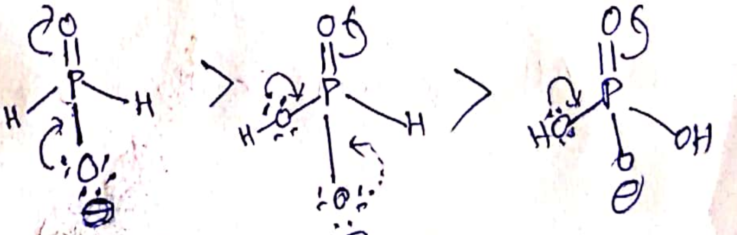
④ ↑'ing the no. P–H bonds $\longrightarrow H_3PO_3 < H_3PO_2 \equiv H_4P_2O_5$

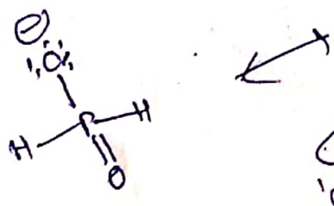
⑤ oxo acids with 2 P=O bonds are ① $H_4P_2O_5$ ② $H_4P_2O_7$ ③ $H_4P_2O_6$

⑥ oxo acid with 3 P=O bonds is $(HPO_3)_3$

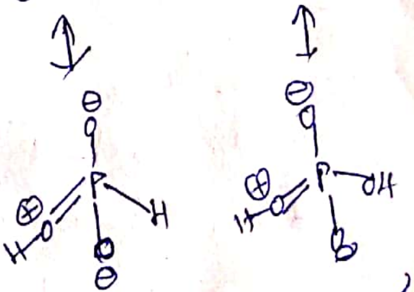
Acidic strength :– $H_4P_2O_7 > H_3PO_2 > H_3PO_3 > H_3PO_4$
(Ka = High)

stability of conjugate bases :–





(–ve charge on 'O' atom stabilised by Resonance)



Due to cross-conjugation b/w –OH grp & P=O, –ve charge on 'O' atom not stabilise.