VA GROUP ELEMENTS

- General configuration : $ns^2\ np^3$
- These are also called as pnicogens / pilogens as their hydrides are suffocating and poisonous

metalloid

$\underbrace{N \quad P}_{\text{non-metals}} \quad As \quad \underbrace{Sb \quad Bi}_{\text{metals}}$

- **Atomicity:** Number of atoms in a molecule
- N : diatomic (N_2)
- P, As, Sb : tetra atomic (4)
- Bi : monoatomic
- **Reasons for the difference in atomicities**
- General valency of these elements is 3
- ‘N’ satisfies its valency through triple bond
- The large size of other elements donot permit them to form multiple bonds. To satisfy the trivalency they exist as tetra atomic molecules
- **Physical state:**
- N_2 - gas ; others - solids
- **Reasons for the difference in Physical states**
- Due to diatomic form M.wt of N_2 is less
- London forces are weak, therefore it is gas
- The high atomicity of other elements increase their mol.wt, london forces become strong hence, they become solids
- **Catenation:**
- In V group, N_2 has high catentation tendency
- Catenation of N_2 = 7 atoms
- Catenation of P = 2 atoms (P–P)
- **Allotropy:**
- Except Bi all others exhibit allotropy

N_2 : $\alpha - N_2 \xrightleftharpoons{-238.5°C} \beta\text{-}N_2$

- P : white / yellow, red, α -black, violet scarlet
- As: Grey, yellow, black
- Sb: yellow, black, explosive
- **White phosphorus :** (yellow)
- When exposed to air a layer of red 'P' gets deposited an white 'P' & it appears to be yellow in colour, Hence called as yellow phosphorus
- It is the most reactive allotrope
- Most poisonous allotrope (as Zn_3P_2 it is used as rat poison)
- It is stored in water due to its low iginition temperature (31.8°C)
- It exhibits phosphorescence. (bones will glow in dark as bones contain phosphate unit)
- **Red phosphorus:**
- Less reactive allotrope & more stable
- As P_4S_3, red 'P' is used in match sticks
- **Black phoshorus:**
- It is thermodynamically stable allotrope of 'P'
- Structure is similar to graphite
- It is the conductor of electricity
- It is the least reactive allotrope of 'P'

Q. Why white phosphorus is more reactive than red phosphorus ?

Sol: i) Due to the independent tetrahedral structure

ii) the lone pairs on 'P' decrease the bond angle from 90°C to 60°

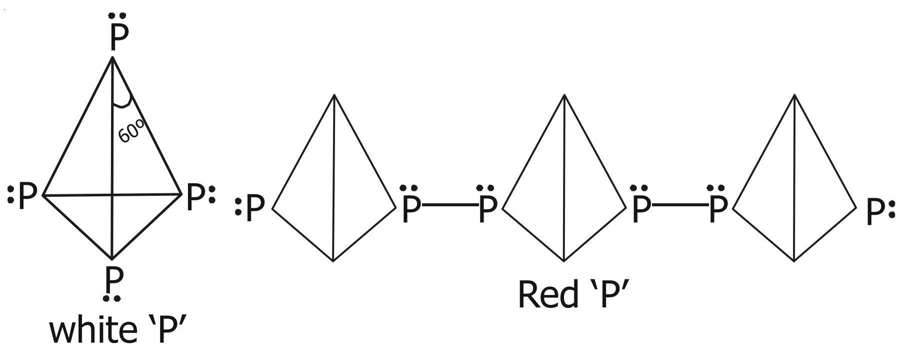
iii) due to the angle strain, white P becomes more reactive

- Red phosphorus is less reactive

i. due to its polymeric structure

ii. the effect of lone pairs on 'P' is distributed among the tetrahedral unts

iii) angle strain is less therefore less reactive



- **Preparation methods of V group elements :**
- **Nitrogen:**
- $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$ • $2NaN_3 \xrightarrow{\Delta} 3N_2 + 2Na$
- $Ba(N_3)_2 \xrightarrow{\Delta} 3N_2 + Ba$ • $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + CrO_3 + 4H_2O$
- $NH_2CONH_2 + 3NaOBr \xrightarrow{\Delta} N_2 + 3NaBr + CO_2 + 2H_2O$
  urea
- $3CaClOCl + 2NH_3 \xrightarrow{\Delta} N_2 + 3CaCl_2 + 3H_2O$
  Bleaching powder (O.A)
- **Phosphorus:**
- $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 6CaSiO_3 + 10Co$
  Phorphate rock
- **Arsenic:** $4\ FeAss \xrightarrow{\Delta} 4FeS + As_4$
  Arsenopyrites
- **Antimony:** $Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS$
  Stibnite
- **Bismuth:** Obtained as a byproduct during the extraction of Pb, Zn or Cu
- **Hydrides of V group elements :**
- General formula – MH_3
- They cannot form pentahydrides due to the less E.N of 'H_2' as H cannot effectively decrease the energy of d-orbital of central atom.

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Ammonia	phosphene	Arsene	stibine	Bismuthine

- **Preparation:** hydrolysis of binary compounds
- $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$
- $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$
- **Hybridisation:** Sp^3 **Structure** : pyramidal
- **Bond angle:** decrease (E.N of central atom decrease)
- **Physical state: all** are poisonous gases
- **Boiling point:** $SbH_3 > NH_3 > AsH_3 > PH_3$
  due to hydrogen bonding
- **volatility:** $PH_3 > AsH_3 > NH_3 > SbH_3$
- **Thermal stability:** decrease (M–H B.E decrease)
- **Reducing action:** increase (M–H B.E decrease)

- **Lewis basicity:** decrease due to the increase in molecular size & the diffusion of lone pair into the vacant d-orbital increase
- **Poisonous nature:** increase as M–H B.E decrease
- **Oxides of V group:** $\xrightarrow{M_2O_3,\ M_2O_4,\ M_2O_5}$ acidity increase as oxidation state increase and oxidising action increase as oxidation state increase
- Pentoxides are stronger oxidation agents. Among them N_2O_5 is the stronger oxidising agent due to its smaller size (In similar oxidation states generally smaller ion behaves as strong oxidising agent)
- P_2O_5 behaves as oxidising agent in dry conditions. In moist conditions P_2O_5 prefers to behaves as dehydrating agent
- **Oxides of Nitrogen:**

1. Nitrous oxide : N_2O : O.S = +1
2. Nitric oxide : NO : O.S = +2
3. Nitrogen sesqui oxide : N_2O_3 : O.S = +3
4. Nitrogen dioxide : $NO_2 \approx N_2O_4$: O.S = + 4
5. Nitrogen pentaoxide : N_2O_5 : O.S = +5

- **Geneal Characters of oxides of Nitrogen:**

i. **Neutral oxides:** N_2O, NO

ii. **Acidic oxides:** $\xrightarrow[\text{acidity increase (oxidation state increase)}]{N_2O_3,\ N_2O_4,\ N_2O_5}$

iii. **Sesqui / mixed oxides:** $N_2O_3 \longrightarrow (NO + NO_2)$

iv. **Laughing gas :** N_2O it also used as local anesthetic in dental surgery

v. **Oxides with odd e^-:** NO_2, NO

vi **Coloured oxides :** NO_2 is reddish brown, N_2O_3 is blue in colour, N_2O_5 is yellow in colour due to impurity

vii. **Oxides that dimerise :**

$$2NO \rightleftharpoons N_2O_2 \text{ (liq \& solid)}$$

$$\underset{\substack{\text{reddish brown}\\ \text{paramagnetic}}}{2NO_2} \xrightleftharpoons{\text{Room temp.}} \underset{(g)}{N_2O_4} \xrightleftharpoons{-11.2°C} N_2O_{4\,(S)}$$

colourless
diamagnetic

viii. **Paramagnetic oxides :**

NO in gaseous state ; NO_2 as monomer

- **Oxides that dissociate:**

$$N_2O_3 \rightleftharpoons NO + NO_2 \text{ (liquid \& gaseous state)}$$

$$N_2O_5 \underset{\text{temperature}}{\overset{\text{room}}{\rightleftharpoons}} N_2O_4 + \tfrac{1}{2} O_2$$

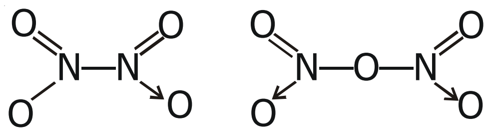
$$N_2O_4 \rightleftharpoons 2NO_2$$

ix. **Oxides that ionise:**

$$N_2O_4 \rightleftharpoons NO^+ NO_3^- \text{ (liquid \& solid states)}$$

$$N_2O_5 \rightleftharpoons NO_2^+ NO_3^- \text{ (solid)}$$

- In solid state resonance is not observed to stabilize themselves the oxides undergo ionisation



- In the above oxides resonance is observed between dative bond and double bonded oxygen
- **Acid anhydrides:** $N_2O_3 + H_2O \longrightarrow 2HNO_2$ (nitrous acid)

$$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \text{ (nitric acid)}$$

- **Preparation of oxides of Nitrogen :**
- N_2O: $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

$NO \rightarrow Cu + \text{dil.}HNO_3$

$N_2O_3 \rightarrow Cu + 6NO + HNO_3$ NO: $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

$NO_2 \rightarrow Cu + \text{ conc } HNO_3$ N_2O_3: $2Cu + 6HNO_3 \rightarrow 2Cu(NO_3)_2 + NO + NO_2 + 3H_2O$

N_2O_3

NO_2: $Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$

N_2O_5: $2HNO_3 \xrightarrow[210^\circ C]{P_2O_5} N_2O_5 + 2HPO_3$ (dehydrating agent)

- **Special methods of preparation of oxides of Nitrogen :**

NO: **Ostwad's process: (Catalytic / partial oxidation of NH_3)**

$$4NH_3 + 60_2 \xrightarrow[\text{6 atom Pt/Rh}]{750^\circ C} 4\ NO + 6H_2O$$

NO_2: (decomposition of heavy metal nitrates like Ba, Pb, Hg, Ag)

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$$

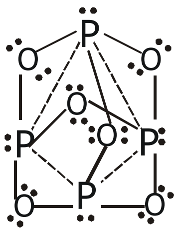
Oxides of phosphorus: P_4O_6 P_4O_8 P_4O_{10}

- Phosphorus oxides dimers as 'P' cannot form the stable π bond with oxygen
- **Preparation:** $P_4+3O_2 \xrightarrow{\Delta} P_4O_6$

  $4P_4O_6 \longrightarrow 3P_4O_8+4P$

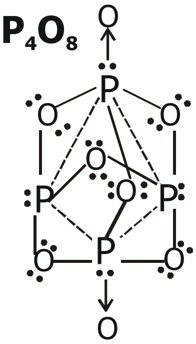
  $P_4+5O_2 \longrightarrow P_4O_{10}$
- **Hydrolysis:** $P_4O_6 + 2H_2O \rightarrow 4HPO_2 \xrightarrow{+2H_2O} 2H_4P_2O_5 \xrightarrow{+2H_2O} 4H_3PO_3$
- $P_4O_{10} + 2H_2O \rightarrow 4HPO_3 \xrightarrow{+2H_2O} H_4P_2O_7 \xrightarrow{+2H_2O} 4H_3PO_4$
- $P_4O_8 + 6H_2O \rightarrow 2H_3PO_3 + 2H_3PO_4$
- **Structure:**
- **Basic unit:** consists of 4 'P' atoms at the 4 corners of tetrahedraon

P_4O_6



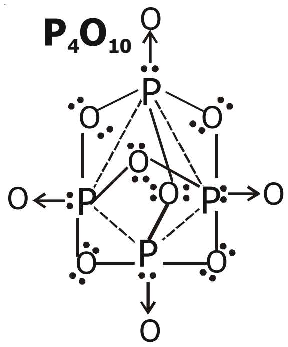
P=+3
0=-2
P-P=0
P-0-P=6
P-0=12
P→O=0

P_4O_8



2P=+5
2P=+3
0=-2
P-P=0
P-0-P=6
P-0=12
P→O=12

P_4O_{10}



P=+5
0=-2
P-P=0
P-0-P=6
P-0=12
p→O=4

- **Oxyacids of phosphorus:** In V group, 'P' forms more number of oxyacids due to :

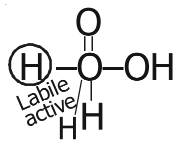
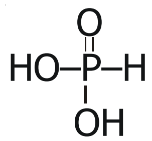
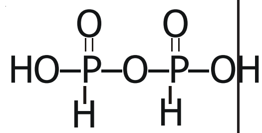
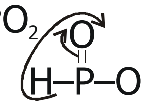
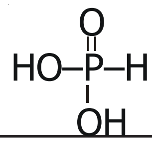
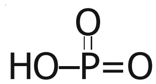
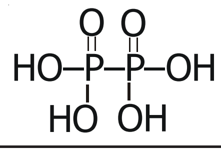
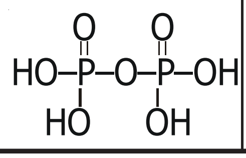
i. The ability to form π bond or dative bond with 'O' with resonance between those two bonds

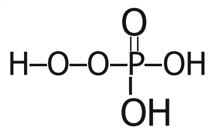
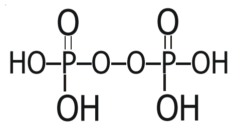
ii. Presence of vacant at orbitals due to which it can exhibit variable oxidation state

iii. The catenation tendency of 'P' to the extent of 2 atoms (P–P)

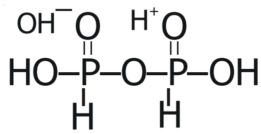
- 'P' forms three series of oxyacids

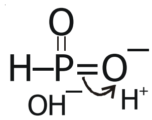
  i. Phosphorous acid series ii. Phosphoric acid series iii) Peroxy acid series
- Differs from the oxyacids of 'S' as it canot form self linked oxyacids.

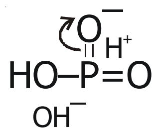
Sl.No.	Name	formla	O.S	Basicity	Slats
I	**Phosphorous acid**	**series**			
1.	Hypophosphorous	H_3PO_2	+1	1	$H_2PO_2^-$
	or phosphinic acid				
2.	Phosphorous (or)	H_3PO_3	+3	2	$H_2PO_3^-$
	phosphonic acid				HPO_3^{-2}
3.	Pyrophosphorous	$H_4P_2O_5$	+3	2	$H_3P_2O_5^-$
	diphosphorous				$H_2P_2O_5^{-2}$
4.	Metaphoshorous	HPO_2 	+3	1	PO_2^-
II.	**Phosphoric acid series:**				
1.	Ortho phosphoric	H_3PO_4	+5	3	$H_2PO_4^-$
	or phosphoric				HPO_4^{-2}, PO_4^{-3}
2.	Metaphosphoric (or)	HPO_3	+5	1	PO_3^-
	glacial phosphoric				
3.	Hypophosphoric	$H_4P_2O_6$	+4	4	$H_2P_2O_6^{-2}$
					$HP_2O_6^{-3}$, $P_2O_6^{-4}$
4.	Pyrophosphoric (or)	$H_4P_2O_7$	+5	4	$H_2P_2O_7^{-2}$
	diphophoric acid				$P_2O_7^{-4}$

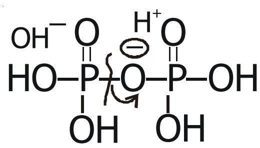
III.	**Peroxy acid series:**			
1.	Peroxymono phosphoric acid	H_3PO_5 	+5	3
2.	Peryoxy diphosphoric acid	$H_4P_2O_8$ 	+5	4

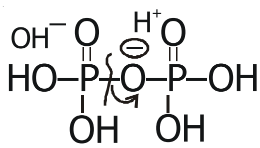
- **Products of hydrolysis :**

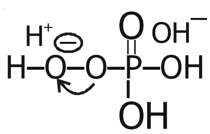
1. Pyro phosphorous aicd$H_4P_2O_5$  $\rightarrow H_3PO_3 + H_3PO_3$

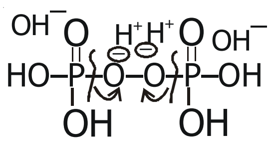
2. Metaphosphorous acid HPO_2  $\rightarrow H_3PO_3$

3. Metaphosphoric acid PHO_3  $\rightarrow H_3PO_4$

4. Hypophosphoric acid $H_4P_2O_6$  $\rightarrow H_2PO_3 + H_3PO_4$

5. Pyrophosphoric acid H $H_4P_2O_7$  $\rightarrow 2H_3PO_4$

6. Peroxymonophosphoric acid H_3PO_5  ® $H_3PO_4 + H_2O_2$

7. Peroxydiphosphoric acid $H_4P_2O_8$  ® $2H_3PO_4 + H_2O_2$

Q. Possible methods of prepartion of phosphorus acids diphosphorous acid,
H_3PO_3 $H_4P_2O_5$
Phosphopric, hypophosphoric, diphosphoric, peroxymonophosphoric,

H_3PO_4 $H_4P_2O_6$ $H_4P_2O_7$ H_3PO_5

Peroxodiphoric acdis $H_4P_2O_8$

- **Phosphorous acid (H_3PO_3)**

$H_4P_2O_5 \xrightarrow{H_2O} 2H_3PO_3$ $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

Pyrophosphorous acid $P_4O_6+6H_2O \rightarrow 4H_3PO_3$

$HPO_2, \xrightarrow{H_2O} H_3PO_3$ **Diphosphorous acid:** ($H_4P_2O_5$)

Metaphosphorous acid $2H_3PO_2 \xrightarrow[\Delta]{H_2O} H_4P_2O_5$

$H_4P_2O_6 \xrightarrow{H_2O} H_3PO_3+H_3PO_4$ $P_4O_6+H_2O \rightarrow 2H_4P_2O_5$

Phosphoric acid (H_3PO_4): $H_3PO_5 + H_2O \rightarrow H_3PO_4 + H_2O_2$

$HPO_3 \xrightarrow{H_2O} H_3PO_4$ $H_4P_2O_8 + H_2O \rightarrow 2H_3PO_4 + H_2O_2$

Metaphosphoric acid

$H_4P_2O_6 \xrightarrow{H_2O} H_3PO_4+H_3PO_3$ $POCl_3+3H_2O \rightarrow H_3PO_4$

Hypophosphoric acid $P_4O_{10} + 6H_2O+O_2 \rightarrow 4H_3PO_4$

$H_4P_2O_7 \xrightarrow{H_2O} 2H_3PO_4$ $P_4O_8 + 6H_2O+O_2 \rightarrow 4H_3PO_4$

Pyrophosphoric acid

$H_4P_2O_6$ (hypophosphoric acid: Diphosphoric acid ($H_4P_2O_7$):

$H_3PO_3 +H_3PO_4 \xrightarrow[\Delta]{H_2O} H_4P_2O_6$ $2H_3PO_4 \xrightarrow{-H_2O} H_4P_2O_7$

$P_4O_8+4H_2O \rightarrow 2H_4P_2O_6$ $Pb_2P_2O_7+4CH_3COOH \rightarrow 2Pb(CH_3COO)_2$

$H_3PO_4 + H_3PO_3$ ® $H_4P_2O_7 + H_4P_2O_7$

Peroxymonophosphoric acid (H_3PO_5): Peroxydiphosphoric acid ($H_4P_2O_8$):

$PCl_5+H_2O_2+H_2O \rightarrow H_3PO_5$ $H_4P_2O_7 + H_2O_2+H_2O \rightarrow H_4P_2O_8$

- **Oxyacids of Nitrogen:**

1. Hyponitrous : $H_2N_2O_2$ 2. Nitrous : HNO_2
3. Nitric : HNO_3 4. Pernitric : HNO_4

1. **Hyponitrous acid preparation:** $Ag_2N_2O_2$

$$Ag_2N_2O_2 \xrightarrow{\text{Dil.HCl}} 2AgCl + H_2N_2O_2$$

$$Ag_2N_2O_2 \xrightarrow{H_2S} Ag_2S + H_2N_2O_2$$

- The acid is highly unstable hence decomposes

  $H_2N_2O_2 \rightarrow N_2O + 2H_2O$

2. **Nitrous acid:** Nitrous acid exists only in solution state. Hence anhydrous HNO_2 cannot be prepared

   Preparation: $Ba(NO_2)_2 + \text{dil.}H_2SO_4 \rightarrow BaSO_4 + 2HNO_2$

   ice cold

- In solution state also HNO_2 is unstable hence it decomposes. The products of decomposition are decided by the concentration of the solution.

  dilute solution: $3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O$

  Oxidation

  Reduction

  Concentrated solution: $2HNO_2 \rightarrow N_2O_3 + H_2O$

- In dil. solution HNO_2 undergoes disproportionation. Hence it can behave as both oxidising & reducing agent

  Reducing action: $HNO_2 + (O) \longrightarrow HNO_3$

$NO_2^- \xrightarrow{KMnO_4/H^+} Mn^{+2}$ colourless

$NO_2^- \xrightarrow{K_2Cr_2O_7/H^+}$ orange red $\;Cr^{+3}$ green

$NO_2^- \xrightarrow{Br_2S\ \text{water}}$ reddish brown $\;Br^-$ colourless

$NO_2^- \longrightarrow NO_3^-$

- **Oxidising action: $2HNO_2 \longrightarrow 2NO + H_2O + (O)$**

turns starch iodide paper blue
(KI + CH_3COOH+starch)

$NO_2 + I^- \longrightarrow NO + I_2 + \text{starch}$

$FeSO_4 \longrightarrow Fe_2(SO_4)_3$

$Na_3AsO_3 \longrightarrow Na_3AsO_4$

sod. Arsenite — sod. arsenate

$Sn^{+2} \longrightarrow Sn^{+4}$

Stannite ion — stannate ion

3. **Nitric acid (HNO_3):** can be manufactured by two methods:

i. **Ostwald's process : (partial / catalytic oxidation of NH_3)**

$$4NH_3 + 5O_2 \xrightarrow[\text{6 atom Pt/Rh}]{750°C} 4NO + 6H_2O + 21.6\ \text{kcal/mole}$$

$2NO + O_2 \longrightarrow 2NO_2$

$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$ recycled. again

ii. **Berkland – Eyde Process:**

$N_2 + O_2 \xrightleftharpoons{3000\ K} 2NO - 43.2$ kcal

$2NO_2 + O_2 \longrightarrow 2NO_2$

$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$

- Nitric acid (HNO_3) is generally considered as **aquafortis (strong water)** as it can oxidise most of the elements in periodic table
- Nitric acid can behave as an acid, an oxidising agent & it differs H_2SO_4 as it cannot behave as dehydrating agent
- As an acid HNO_3 neutralises metal oxides metal hydroxides, metal sulphites, metal carbonates etc to the respective metal nitrates.
- When it behaves as an oxidising agent it may get reduced to ammonium nitrate (NH_4NO_3) or nitrous oxide (N_2O) or nitric oxide (NO) or nitrogen dioxide (NO_2) or nitrogen (N_2) these products of reduction depend on

i. concentration of the acid

ii. Nature of the element to be oxidised

iii. temperature of the reaction

I. **Oxidation of non metals / metalloids: HNO_3 oxidises them to their highest oxyacids: Eg:** C, P, S, I, Sn

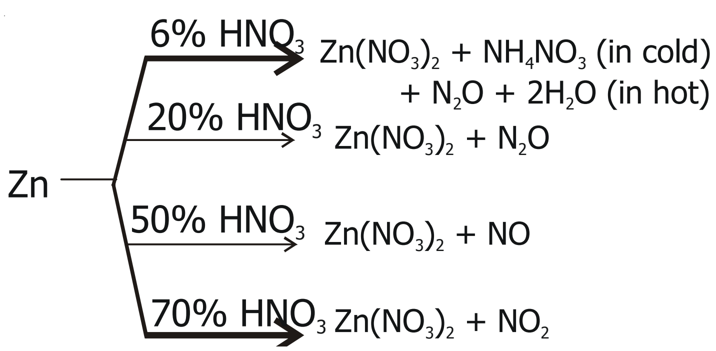
$P + 5HNO_3 \rightarrow H_3PO_4 + 5NO + H_2O$

$C \rightarrow H_2CO_3$: $S \rightarrow H_2SO_4$; $I \rightarrow HIO_3$; $Sn \rightarrow H_2SnO_3$

II. **Oxidation of metals which are above H_2 in electrochemical series:**

Eg: (Mg, Mn, Fe, Zn)

- Very dil. HNO_3 (2%) :
- $Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2$



III. **Oxidation of metals which are below H_2 in electrochemical series:**

Eg: (Cu, Ag, Au, Hg, Pt)

- Cu + hot conc $HNO_3 \longrightarrow Cu(NO_3)_2 + N_2$
- Hg + HNO_3
  - $\xrightarrow{dil}$ $Hg_2(NO_3)_2 + NO$ Mercurous nitrate
  - $\longrightarrow$ $Hg(NO_3)_2 + NO_2$ Mercuric nitrate

IV. Action on noble metals : **Eg:** Au, Pt, Ir, Pd

- Noble metals donot dissolve in nitric acid but they readily dissolve in aquaregia due to the formation of respective cloro complexes.
- **aquaregia:** Conc HNO_3 + conc.HCl

  1 : 3

- Au $\rightarrow$ H $[AuCl_4]$
- Pt $\rightarrow$ H_2 $[PtCl_6]$
- Pd + dil.$HNO_3 \rightarrow Pd(NO_3)_2$
- Ir + aquaregia $\rightarrow$ no reaction

V. **Action on sugar:**

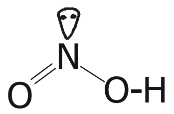
$C_{12}H_{22}O_{11} + HNO_3 \rightarrow (COOH)_2$ oxalic acid

- **Pernitric acid:**

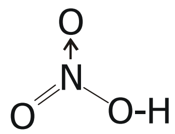
  Preparation: $NaNO_3 + H_2O_2 + H_2O \rightarrow NaNO_4 + 2H_2O$

- **Structures of oxyacids of N_2:**

HNO_2:
hybridisation Sp^2:
structure : Angular

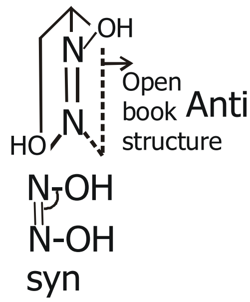


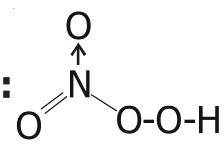
HNO_3
hybridization Sp^2:
structure:



$H_2N_2O_2$:
hybridization: Sp^2
structure:

angular around N_2



- **HNO_4 (pernitric acid) : Hybridistion :** Sp^2 **structure tp:** 
- **Halides of V group Elements:**
- **Trihalides: (MX_3)**
- **Preparation :** $2M + 3X_2 \rightarrow 2MX_3$
- **Hybridisation :** Sp^3 **structure :** Py

- **Bond angle:** bond angle decrease (E.N of C.A decrease)

$$\xrightarrow{NX_3 \; < \; PX_3 \; < \; AAX_3 \; < \; SbX_3 \; < \; BiX_3}$$

Stability increase as +3 stability increase due to inert pair effect

- **Stability:** NF_3 stable, $\underbrace{NCl_3 \quad NBr_3 \quad NI_3}_{\text{unstable}}$
  1. low N-X bond polarity
  2. low –X bond energy

- **Lewis basicity:** :

$$\xrightarrow{NX_3 \; > \; Px_3 \; > \; AAX_3 \; > \; SbX_3 \; > \; BiX_3}$$

Decreasing order of lewis basicity as e^- density decrease due to increase in molecular size

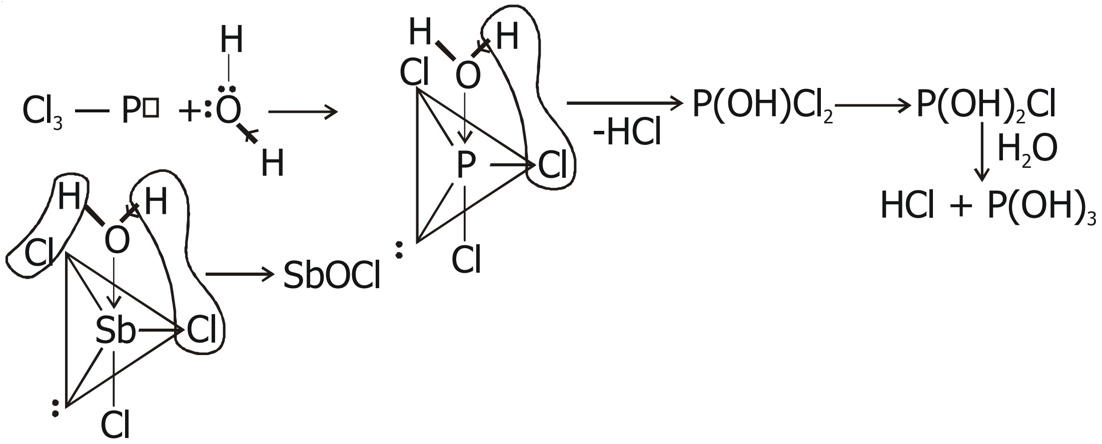
$$\xrightarrow{NF_3 < NCl_3 < NBr_3 < NI_3}$$

Lewis basicity increase (as E.N of suounding atom decrease & the e^- density on N increase

- **Hydrolysis:**
- Except NF_3, PF_3, PF_5 all others are hydrolysed
- NF_3 doesnot undergo hydrolysis due to the absence of vacant orbital with N & F. However, it is hydrolysed under elevated conditions with steam

$$NF_3 + \underset{\text{steam}}{3H_2O} \xrightarrow{\text{elevated condition}} N_2O_3 + 6HF$$

- PF_3 & PF_5 are resistant towards hydrolysis as the P–O bond energy (hydration energy) is less than P–F bond energy due to backbonding
- $NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$
- $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
- $AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + 3HCl$
- $SbCl_3 + 3H_2O \rightarrow SbOCl + 2HCl$
- $BiCl_3 + 3H_2O \rightarrow BiOCl + 2HCl$
- NCl_3 when hydrolysed NH_3 is liberated instead of HNO_2 due to inability of N_2 to form bond with H_2O molecule as it has no vacant orbital
- P & As interact with H_2O molecule by using their vacant d-orbitals. Hence they form the respective -ous acids.
- Sb & Bi due to the high polarising power form oxychlorides



- **Pentahalides:** (MX_5)
- 'N' cannot form pentahalides due to the absence of vacant orbitals
- P : PF_5. PCl_5, PBr_5 exist but not PI_5 due to steric hinderance
- As : AsF_5, $AsCl_5$ ($AsCl_5$ decomposes at 30°C)
- Sb: SbF_5 $SbCl_5$
- Bi : BiF_5 due to high E.N of Cl the d orbitals is activated in Bi hence it forms BiF_5
- **Preparation:** $MX_3 + X_2 \rightarrow MX_5$
- **Hybridistaion:** Sp^3d **structure :** tbp
- **Bond angle:** 90°, 120°, 180° (any molecule with mulptiple bond angles is highly unstable but these penta halides are stable due to Pseudoberry rotation

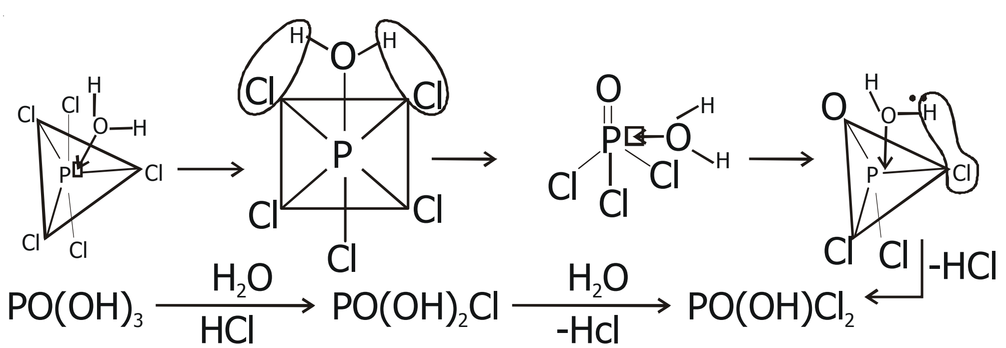
  In solid state : $2PCl_5 \rightarrow PCl_4^+ PCl_6^-$

  $PBr_5 \rightarrow PBr_4^+ Br^-$
- **Hydrolysis:**

  $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

  $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

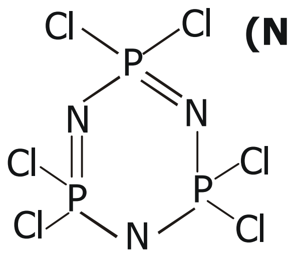
  $POCl_3 + 3H_2O H_3PO_4 + 3HCl$



- **Phosphazenes:**
- Linear or cyclic polymers of $[NPCl_2]_n$ group

  phosphazene $\rightarrow$ phosph-phosphorous + Az-nitrogen + en-unsaturation
- Each $[NPCl_2]$ is considered as phosphonitrilic chloride (o) phosphazene (or) dichloro phosphazene
- **Nomenclature:** root word = phosphonitrilic chloride
- The number of times the unit is repeated is indicated with -di, tri, tetra etc $(NPCl_2)_3$ – tri (phosphonitrilic chloride)

  $(NPCl_2)_4$ – tetra (phosphonitrilic chloride)



$(NPCl_2)_3$

O.S

P=+5

N=-3

Cl=-1

Hybridisation

P=Sp^3

N=Sp^2

Preparation

$$nPCl_5 + nNH_4Cl \left\{ \begin{array}{l} \xrightarrow[C_2H_4Cl_2 \text{ or } C_6H_5Cl]{\text{Inert solvent}} \\ \xrightarrow{145\text{–}160°} \end{array} \right\} \rightarrow [NPCl_2]_n + 4nHCl$$