Group 15 elements [Pnicogens - VA]

⇒ Element	At·no	Ele· config
N	7	$[He]\,2s^2\,2p^3$
P → most abundant element	15	$[Ne]\,3s^2\,3p^3$
As	33	$[Ar]\,3d^{10}\,4s^2\,4p^3$
Sb	51	$[Kr]\,4d^{10}\,5s^2\,5p^3$
Bi	83	$[Xe]\,5d^{10}\,6s^2\,6p^3$
Mc	115	$[Rn]\,7s^2\,7p^3$

→ 11th **Most** abundant element in the Earth crust → Phosphorous (P).

→ G.E.C → ns^2np^3.

→ Abundance order → P > N > As > Sb > Bi.

→ N_2 present in the air to the extend of 78% by volume and 80% by mass.

→ N_2 as nitrates KNO_3, $NaNO_3$.

→ Except 'P' other elements are avaliable in free state.

→ Phosphorous are present in animals, plants, living cells & bones.

* Phospho proteins are present in milk and egg.

→ Phosphorus is avaliable in & as

Phosphorite : $Ca_3(PO_4)_2$

Fluorapatite : $3Ca_3(PO_4)_2 \cdot CaF_2$

Chlorapatite : $3Ca_3(PO_4)_2 \cdot CaCl_2$

Hydroxapatite : $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$

→ General Properties

Atomicity :→ (AM)

N_2 - diatomic

P_4, As_4, Sb_4 - tetraatomic

Bi - monoatomic

→ Physical state :

N_2 - gas

P_4, As_4, Sb_4 - solid

Bi - solid

→ Metallic nature (MN)

N and P → non metals

As and Sb → metalloids

Bi → metal

→ Covalent radius

$N < P < As < Sb < Bi$

→ I.P (Ionization potential)

$N > P > As > Sb > Bi$

→ Electronegativity (EN)

$N > P > As > Sb \simeq Bi$

→ Melting point (M.P):

$N < P < Bi < Sb < As$

→ Density ($d = M/V$) :

N(at 63k) $< P < As < Sb < Bi$

→ Boiling point (B.P):

$N < P < As < Bi < Sb$

→ Oxidation states :

The charge present on atom "$-3, +3, +5$".

* The ability to exhibit +5 oxidation state, Bi → +3

* $6s^2\ 6p^3$ due to inert pair effect

* Bi only exhibits +5 in BiF_5 others As, Sb, Bi = -3 does not exhibit easily.

Nitrogen : [-3 to $+5$ oxidation state]

* $NH_3 = -3$

* $NH_2-NH_2 = -2$
(hydrazene)

* $NH_2OH = -1$
hydroxy amine

* $N_2 = 0$

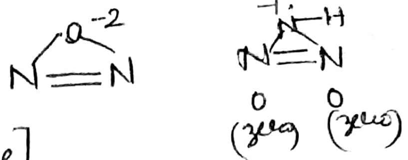
* NO_2 (or) $N_2O_4 = +4$
nitrogen dioxide

* N_2O_5 (or) $HNO_3 = +5$
nitric oxide (or) nitric acid

N_2O_3 (or) $HNO_2 = +3$

* $N_3H = -1/3$
Hydrazoic acid

* $N_2O = +1$



nitrous oxide

[+1 to +4 oxidation state]

→ Nitrogen(N) undergoes disproportionation in acidic medium.

$$3H\overset{+3}{N}O_2 \longrightarrow H\overset{+5}{N}O_3 + H_2O + 2\overset{+2}{N}O$$

① $H_3PO_2 = +1$ hypophosphorus acid

② $H_3PO_3 = +3$ orthophosphorous acid

③ $H_3PO_5 = +5$ orthophosphoric acid

④ $PH_3 = -3$ phosphine

In acidic and alkaline medium:

$$4H_3\overset{+3}{P}O_3 \longrightarrow 3H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$$

Catentation capacity:

$C-C \Rightarrow 345\ kJ/mole > \underset{201}{P-P} > \underset{167}{N-N} > \underset{146}{As-As}$

Allotrophy:

→ Except "N" all other elements exhibits allotrophy.

→ Phosphorous exhibit as

i) white phos.

ii) Red P

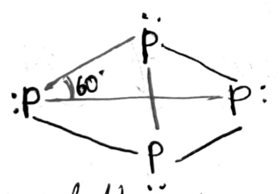
iii) Black P

iv) violet P.

i) White P :→ contains P_4 units

→ Translucent waxy solid

→ stored under water

→ 

no. of P–P bonds = 6

→ This is most reactive form of phosphorous

→ This is insoluble in water but readily soluble in CS_2.

→ Glow in dark (Chemiluminiscence).

$\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow \overset{-3}{PH_3} + 3NaH_2\overset{+1}{PO_2}$

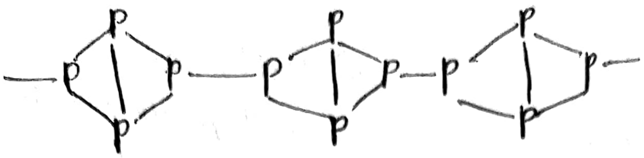
Sodium hypo phosphite

↓

(disproportionation reaction) → undergoes both oxidation & reduction

ii) Red P :

$(P_4)_n$



* When white P (P_4) is heated at 573K then Red P (P_4) is formed
3days

* Less reactive.
* Insoluble in H_2O & CS_2.
* Not glow in dark.

iii) Black P :

It has graphite like structure.

→ Two types of black P ⇒ α-black, β-black

* When red P $\xrightarrow{803K}$ α-black is formed.
* When white P $\xrightarrow{473K}$ β-black is formed.
* Thermodynamically most stable β-Black P.
* Good conductor of electricity.

As : Metallic (or) green.

Non metallic (yellow)

Black

Sb : Metallic and explosive form

Anamalous behaviour of N :

Nitrogen (N) : 1. Has small size.

2. Has high I.P value

3. Has high E.N value

4. Due to the absence of d-orbitals

nitrogen has ability to form pπ-pπ bonds with C and O, while other forms like phosphorous forms dπ-pπ bonds.

5) N_2 is diatomic.

$N \equiv N \rightarrow 1\sigma$ and 2π

It has high bond energy (945.4 kJ/mole) due to it's high B.E, it is less reactive.

6) Preparations :

i) Commercially 'N' is prepared by air by liquification & fractional distillation of air

N_2 [77.2K - B.P]

O_2 [90K - B.P]

ii) In laboratory N_2 is prepared when ammonium chloride is heated with sodium nitrite.

$$NH_4Cl + NaNO_2 \longrightarrow NaCl + 2H_2O + N_2$$

ammonium chloride, sodium nitrite

along N_2, NO and HNO_3 to removes this it is passed through aq. soln of $H_2SO_4 + K_2Cr_2O_7$

iii) Thermal decomposition :

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

ammonium dichromate

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

ammonium nitrite

$$2NI_3 \xrightarrow{\Delta} N_2 + 3I_2$$

iv) Pure form of N_2 is prepared from azide.

$$2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2$$

Sodium azide

$$Ba(N_3)_2 \xrightarrow{\Delta} 2Ba + 3N_2$$

Barium azide

v) <u>From NH_3:</u>

$$2NH_3 + 3CuO \xrightarrow{\Delta} N_2 + 3Cu + 3H_2O$$

$$8NH_3 + 3Cl_2 \xrightarrow{\Delta} N_2 + 6NH_4Cl$$

vi) <u>Properties:</u> → Dinitrogen is colourless, odourless, non-toxic gas.

→ It has low solubility in water.
[2 3.2 cm^2 per lit at 273K and 1 bar]

→ It has low F.P & B.P

→ It has two isotopes $_7N^{14}$ $_7N^{15}$

→ N_2 has high B.E and less reactive
(945.4 kJ/mole)

→ Dinitrogen reacts with metals like

$$6Li + N_2 \xrightarrow[\text{temp}]{\text{high}} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$$

→ Dinitrogen reacts with non-metals like

$$N_2 + O_2 \rightleftharpoons 2NO.$$

<u>Preparation of NH_3:</u>

Haber's process:

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta H = -92.2\ kJ/mole$$

$$\underbrace{CaC_2 + N_2 \xrightarrow{1000^\circ C} CaCN_2 + C}_{\text{nitrolim}}\ (\text{graphite})$$

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Calcium cyanamide

$$C_2H_2 + N_2 \xrightarrow[\text{arc}]{\text{electric}} (CN)_2 + H_2$$

acetylene — $(CN)_2$: cyano gas (pseudohalogen)

$2B + N_2 \xrightarrow{\Delta} 2BN$
Boran nitride

Uses : → N_2 used for preparation of NH_3.
→ It is used to produce inert atomsphere.
→ liquid N_2 is used as refrigerant for biological system & food materials.

Hydrides : Group 15 elements forms MH_3 type hydrides

→ NH_3 ammonia
PH_3 phosphine
AsH_3 Arsine
SbH_3 Stibine
BiH_3 Bismuthin

→ Nitrogen also forms N_2H_4 (hydrazone) and N_3H (hydrazoic acid)
→ These hydrides are prepared when metal nitrites, phosphates and arsinates are hydrolyzed with dil. acids.

Mg_3N_2, Ca_3P_2, Zn_3As_2

$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

$Ca_3P_2 + 6HCl \longrightarrow 3Ca(OH)_3 + 2PH_3$

→ Ease of formation
Thermal stability
Bond energy
Bond angle
$\Big\}$ $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

→ These are Lewis bases.
→ Basic nature $= NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.
→ Reducing power
Bond length
$\Big\}$ $= NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

→ NH_3 has abnormally high B.P due to intermolecular hydrogen bonds.

B.P $= PH_3 < AsH_3 < NH_3 < SbH_3$
M.P $= PH_3 < AsH_3 < SbH_3 < NH_3$

→ Preparation of ammonia (NH_3)

① $NH_2-CO-NH_2 + H_2O \rightarrow (NH_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + CO_2 + H_2O$

urea

② Ammonium salts reacted with bases gives NH_3.

$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$

$(NH_4)_2SO_4 + NaOH \rightarrow 2NH_3 + Na_2SO_4 + H_2O$

③ Haber's process

$N_2 + 3H_2 \rightarrow 2NH_3$, $\Delta H = -46.1\ kJ/mole$

In 1:3 ratio the nitrogen & hydrogen are taken.

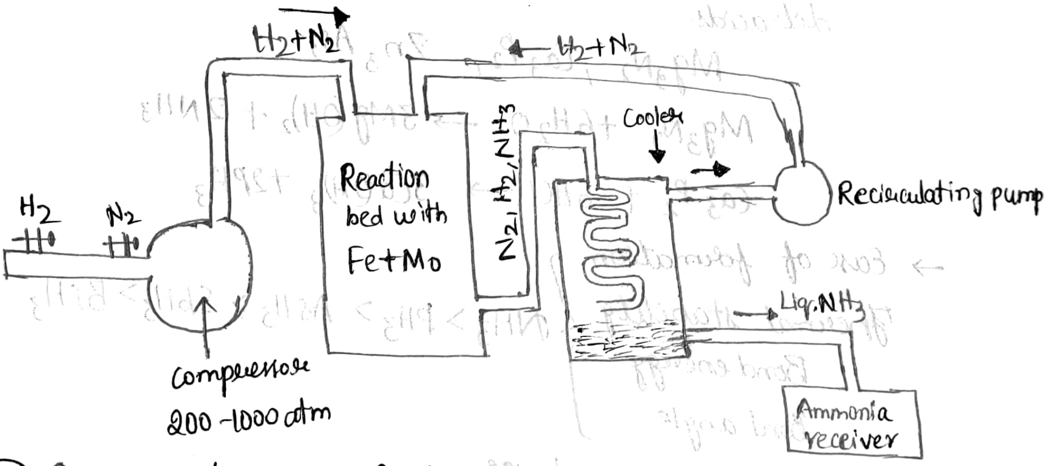
Acc. to Lechatlier the favourable conditions are

temp = 725 – 775 K

press (in atm) = 200 to 500 atm

Catalyst = Fe (or) mixture of $(Fe_2O_3 + FeO) + Al_2O_3 + K_2O$

promoter = Mo



④ Cyanamide process:

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

$CaO + 3C \xrightarrow{2273K} CaC_2 + CO$

CaC_2 ↓ Calcium Carbide

$CaCl_2$ (or) CaF_2 are catalyst.

$CaC_2 + N_2 \xrightarrow{1273K} \underbrace{CaCN_2 + C}_{\text{nitrolim}}$ (graphite)

nitrolim = mixture of Ca cyanamide & graphite

$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$

(5) $NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$

$(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$

$(NH_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + H_2CO_3$

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$

$BN + 3H_2O \rightarrow \underset{\text{boric acid}}{B(OH)_3} + NH_3$

$B_3N_3H_6 + 9H_2O \rightarrow NH_3 + B(OH)_3$

$\left.\begin{matrix}(NH_4)_2HPO_4 \\ (NH_4)H_2PO_4\end{matrix}\right\} \xrightarrow{\Delta} NH_3$

$NH_2CO\text{-}NH_2 + 2NaOH \rightarrow 2NH_3 + Na_2CO_3$

→ Reduction of nitrites and nitrates using Devarda's alloys
[Ca/Al/Zn + NaOH]

$\underset{\text{Nitrate}}{NO_3^-} + 9H^+ \rightarrow NH_3 + 3H_2O$

$\underset{\text{Nitrite}}{NO_2^-} + 7H^+ \rightarrow NH_3 + 2H_2O$

→ NH_3 can be dried by CaO (quicklime) anhyd. $CaCl_2$ & H_2SO_4 are dehydrating agent but can't be used due to it reacts with NH_3.

$CaCl_2 + 8NH_3 \rightarrow CaCl_2 \cdot 8NH_3$

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

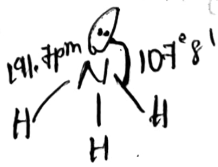
→ Properties :

(i) Ammonium is colourless and pungent odour gas.

(ii) F.P = 195.2 K B.P = 239.7 K

(iii) In liquid & solid state, NH_3 has strong hydrogen bonds

(iv) shape - pyramidal



(v) It is highly soluble in water.

$NH_{3(g)} + H_2O_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$

$2NH_3 \xrightarrow{\Delta} N_2 + 3H_2$

$4NH_3 + O_2 \rightarrow 2N_2 + 6H_2O$

It burns with palegreen flame.

(vi) When it reacts with metal salts it gives

$$ZnSO_4{}_{(aq)} + 2NH_4OH_{(aq)} \longrightarrow Zn(OH)_2{}_{(s)}\downarrow + (NH_4)_2SO_4{}_{(aq)}$$

$$FeCl_3{}_{(aq)} + 3NH_4OH \longrightarrow \underset{ppt}{Fe_2O_3 \cdot xH_2O}\downarrow + 3NH_4Cl$$

(vii) with Cl_2:

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

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

(viii) Oxidising:

$$2\overset{-3}{N}H_3 + 3CuO \rightarrow \overset{0}{N_2} + 3Cu + 3H_2O$$

↓

Reducing agent: PbO & $CaCl_2$

(ix) Forms complexes with transistion metal ions:

$$Cu^{+2}_{(aq)} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{+2} \text{ deep blue}$$

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)}$$

$$AgCl_{(s)} + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$$

(x) with Na

$$NH_3 + Na \xrightarrow{\Delta} \underset{Sodamide}{NaNH_2} + \tfrac{1}{2}H_2$$

$$\downarrow N_2O$$

NaN_3 (sodium azide)

$NaN_3 \xrightarrow{\Delta} N_2$

$NaN_3 \xrightarrow{H_2O} NH_3$

Uses :

① Basic fertilizers

NH_4NO_3 , $(NH_4)_3PO_4$, $(NH_4)_2SO_4$

② Used to prepare HNO_3

③ Liquid NH_3 used as refrigerant.

④ Used to prepare explosives

$$\underbrace{80\%\ NH_4NO_3 + 20\%\ TNT}_{\text{Ammatal}}$$ (Tri Nitro Toluene)

$(NH_4NO_3 + Al)$
Ammonal

→ **Test for NH_3 :**

Brown ppt with Nessler's reagent
↓
$K_2(HgI_4)$
KI & $HgCl_2$ / NaOH (alkaline medium)

white fumes with HCl

$NH_3 + HCl \rightarrow NH_4Cl$

Grey ppt with Hg_2Cl_2

11/4/23 **Phosphine (PH_3)**

1) $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$

2) In atomsphere of CO_2

$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ (sodium hypophosphite)

In laboratory phosphine is prepared by heating P_4 with NaOH in the inert atomsphere of CO_2.

pure form of PH_3 is non-inflammable

impurities P_2H_4 and P_4 - highly inflammable

$PH_3 + HI \rightarrow PH_4I$

impure

$PH_4I + KOH \rightarrow PH_3 + KI + H_2O$

pure

PH_3 colourless gas

Rotten fish like smell

toxic gas

aqueous PH_3 on decomposition gives 'Red P' and H_2.

$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$

$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$

$3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$ Lewis base - $\ddot{P}H_3$

$\ddot{P}H_3 + HBr \rightarrow PH_4Br$

$\ddot{P}H_3 + HI \rightarrow PH_4I$

Uses: → "Holme's signals"

$Ca_3P_2 + CaC_2$ $\quad Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

Spontaneous combustion of phosphine used to produce Holme's signals. Mixture of $Ca_3P_2 + CaC_2$ is used.

$CaC_2 \xrightarrow{H_2O} C_2H_2$

→ Smoke screens are produced by phosphine.

Halides: Group 15 elements forms two types of halides.
(MX_3) Trihalides and pentahalides (MX_5)

Trihalides NCl_3, PCl_3, PF_3, NF_3

Except NF_3 remaining 'N' trihalides are unstable.

1) Low polarity of N−X bond
2) "N−X bond is weak"

$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$

$P_4 + 6Cl_2 \rightarrow 4PCl_3$

Covalent nature except BiF_3

Lewis bases $NX_3 > PX_3 > AsX_3 > SbX_3 > BiX_3$

Basic nature $NF_3 < NCl_3 < NBr_3 < NI_3$

Except NF_3 and PF_3 all halides undergoes hydrolysis.

$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$

$HOCl \rightarrow HCl + [O]$

Coloured + [O] → colourless nascent oxygen [O]

Aq. NCl_3 − Bleaching agent

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$ → orthophosphorous acid

$AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + 3HCl$

$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$ Oxocations are formed

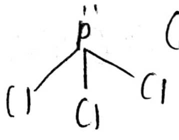
$BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$ (SbO^+Cl^-)

PCl_3: $P_4 + 6Cl_2 \rightarrow 4PCl_3$

$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

Thionyl chloride

P − sp^3



(pyramidal) white oily liquid

$PCl_3 + Cl_2 \rightarrow PCl_5$

$PCl_3 + 3CH_3COOH \rightarrow 3CH_3COCl + H_3PO_3$

$PCl_3 + 3C_2H_5OH \rightarrow 3C_2H_5Cl + H_3PO_3$

$12Ag + 4PCl_3 \rightarrow P_4 + 12AgCl$

Pentahalides - MX_5

PCl_5, PF_5, $SbCl_5$, "BiF_5" - penta halide

* "N" doesn't form NX_5 due to absence of vacant d-orbitals.

$P_4 + 10Cl_2 \rightarrow 4PCl_5$

$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$

Sulphuryl chloride

$PCl_3 + Cl_2 \rightarrow PCl_5$ (yellowish powder) less stable - thermally

$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$

Hydrolysis of PCl_5

$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$

$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$

phosphoric acid

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

→ $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

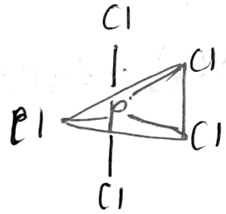
$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$

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

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

PCl_5 P - sp^3d

Trigonal bipyramidal



In solid state PCl_5 exists as $[PCl_4]^+$ $[PCl_6]^-$

$[PCl_4]^+$ ↓ sp^3 Tetrahedral

$[PCl_6]^-$ ↓ sp^3d^2 octahedral

PBr_5 exists as $[PBr_4]^+[Br]^-$

NOTE: PI_5 doesn't exist due to large size of iodine and small electronegative difference b/w phosphorous and iodine.

12/4/23

Oxides: Trioxides Pentaoxides

M_2O_3 M_2O_5 N_2O_5 strong oxidising agent

N_2O_3, P_4O_6 — Acidic

N_2O_5, P_4O_{10} — Acidic

Dimers exists as: P_4O_6, As_4O_6, Sb_4O_6 — Amphoteric

Bi_2O_3 – Basic

Bi_2O_5 pentaoxides are most acidic

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

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

Oxides of nitrogen

N_2O – nitrous oxide

NO – nitric oxide

N_2O_3 – nitrogen seque oxide

NO_2 – nitrogen dioxide

N_2O_5 – nitrogen pentaoxide

Nitrous oxide (N_2O)

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

$$4Zn + 10HNO_3 \text{ (dil)} \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

→ "Laughing gas".

→ Colourless and neutral oxide

$$2N_2O \xrightarrow[\Delta]{800°C} 2N_2 + O_2$$

$$S + 2N_2O \rightarrow SO_2 + 2N_2$$

$$2Mg + 2N_2O \rightarrow 2MgO + 2N_2$$

$$:N \equiv \overset{+}{N} \rightarrow \ddot{O}: \leftrightarrow :\ddot{N} = \overset{(+)}{N} = \ddot{O}$$

$$N \underset{113\,pm}{—} N \underset{119\,pm}{—} O$$

Nitric oxide (NO):

$$4NH_3 + 5O_2 \xrightarrow[1100K]{Pt} 4NO + 6H_2O$$

$$3NaNO_2 + 3H_2SO_4 \longrightarrow 3NaHSO_4 + 2NO + H_2O + HNO_3$$

$$N_2 + O_2 \xrightarrow[arc]{electric} 2NO$$

$$\underset{(dil)}{3M + 8HNO_3} \longrightarrow 3M(NO_3)_2 + 4H_2O + 2NO$$

$M = Cu, Pb, Ag$

→ Colourless gas

→ neutral oxide

→ odd e^- molecule – paramagnetic nature

$$2NO + O_2 \longrightarrow \underset{\text{Reddish brown}}{2NO_2}$$

It oxidises

H_2S to S

$SnCl_2$ to $SnCl_4$

SO_2/H_2O to H_2SO_4

	NO	NO^+ (Nitrosonium ion)
Bond order	2.5	3
Bond length	1.15Å	1.06Å

Bond order $\propto \left(\frac{1}{\text{Bond length}}\right)$

$$2NO + Cl_2 \longrightarrow \underset{\text{nitrosyl chloride}}{2NOCl}$$

$[Fe(H_2O)_5NO]^+$ – Brown Ring complex

Fe +1 Oxidation state

$Na_2[Fe(CN)_5NO]$

$[Ni(CO)_4]$

↓

$[Ni(CO)(NO)_2]$

NO – $3e^-$ donar

CO – $2e^-$ donar

$\dot{\underset{\cdot}{N}} \equiv \ddot{O} \longleftrightarrow :\ddot{N} = \ddot{O}$ N ⋯ O $\underset{115\,pm}{N — O}$

Nitrogen sesque oxide (N_2O_3)

$2NO + N_2O_4 \xrightarrow{250\,K} 2N_2O_3$
2:1

$NO + NO_2 \xrightarrow{-23^\circ C} N_2O_3$

→ Blue solid (or) liquid

→ Acidic oxide

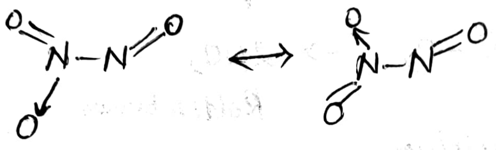
Anhydride of HNO_2 (Nitrous Acid)

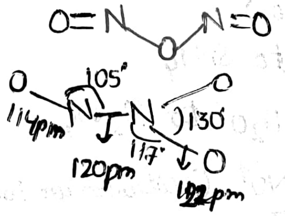
$N_2O_3 + H_2O \rightarrow 2HNO_2$

$N_2O_3 + 2NaOH \rightarrow 2NaNO_2 + H_2O$

Self ionisation

$N_2O_3 \rightarrow NO^+$ and NO_2^-





$N_2O_3 \xrightarrow[\text{temp}]{\text{Room}} NO + NO_2$

Nitrogen dioxide (NO_2)

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

Lead nitrate

$M + \text{con. } HNO_3 \rightarrow M(NO_3)_2 + NO_2 + H_2O$

$M = Cu, Ag, Pb, Zn$

$Sn + \text{con. } HNO_3 \rightarrow H_2SnO_3 + NO_2 + H_2O$
Meta stannic acid

$2NO + O_2 \rightarrow 2NO_2$

→ Reddish brown

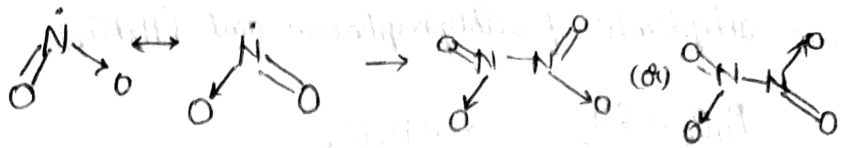
→ odd e^- molecule, paramagnetic.

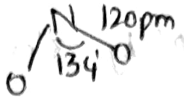
$2NO_2 \rightarrow N_2O_4$ (dimer)

→ colourless, diamagnetic

NO_2 is mixed anhydride of HNO_2 and HNO_3.

$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$





In liquid state it exist as N_2O_4 $NO^+ NO_3^-$

Nitrogen pentoxide (N_2O_5):

$HNO_3 + P_4O_{10} \longrightarrow N_2O_5 + HPO_3$

P_4O_{10} – dehydrating agent.

$4AgNO_3 + 2Cl_2 \longrightarrow 2N_2O_5 + 4AgCl + O_2$
(dry)

N_2O_5 – strong acidic oxide

Acidic nature ⇒ $N_2O < NO < N_2O_3 < NO_2 < N_2O_5$
+1 +2 +3 +4 +5

Anhydride of HNO_3 ($N_2O_5 + H_2O \rightarrow 2HNO_3$)
nitric acid

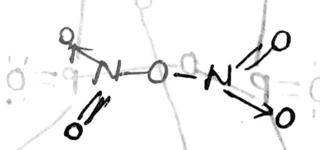
→ N_2O_5 – strong oxidising agent

$I_2 + N_2O_5 \longrightarrow I_2O_5 + N_2$

→ In vapour state – covalent, in solid state – ionic

N_2O_5 as NO_2^+ and NO_3^-

$N_2O_5 + 2NaOH \longrightarrow 2NaNO_3 + H_2O$



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Oxides of phosphorous

Two types

P_4O_6 (phosphorous trioxide)

P_4O_{10} (phosphorous pentoxide)

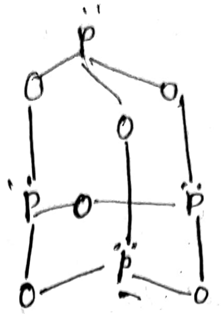
P_4O_6 : $P_4 + 3O_2 \longrightarrow P_4O_6$
white solid

$P_4O_6 + 2O_2 \rightarrow P_4O_{10}$

P_4O_6 anhydride of orthophosphorous acid (H_3PO_3)

$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

In P_4O_6 each "p" by 3"O" atoms



Total no of P-O-P bonds is 6

no of covalent bonds - 12

P_4O_{10} : $P_4 + 5O_2 \rightarrow P_4O_{10}$

Anhydride of phosphoric acid (H_3PO_4)

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

P_4O_{10} - Good dehydrating agent

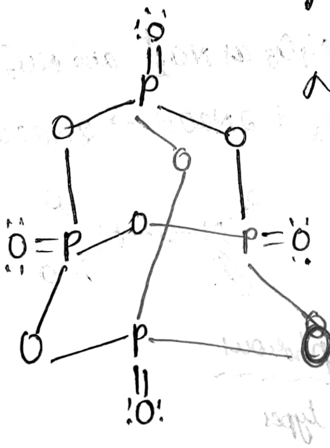
$P_4O_{10} + 4CH_3COOH \rightarrow 2(CH_3CO)_2O + 4HPO_3$

$P_4O_{10} + 2CH_3CONH_2 \rightarrow 2CH_3CN + 4HPO_3$

acetamide

$P_4O_{10} + H_2SO_4 \rightarrow SO_3 + 4HPO_3$

Each 'p' surrounded by 4 'O' atoms



No of P-O-P bonds - 6

Total no. of covalent bonds = 16

OXO acids of nitrogen

1) Hyponitrous acid – $H_2N_2O_2$ (or) HNO
2) Nitrous acid – HNO_2
* 3) Nitric acid – HNO_3
4) pernitric acid – HNO_4

Hyponitrous acid $H_2N_2O_2$

$HO-N=N-OH$

Pernitric acid (HNO_4)

$HO-O-N(\rightarrow O)=O$

peroxy bond

Nitrous acid (HNO_2)

$Ba(NO_2)_2 + H_2SO_4 \rightarrow 2HNO_2 + BaSO_4$

$N_2O_3 + H_2O \rightarrow 2HNO_2$

$NH_3 + H_2O_2 \rightarrow HNO_2 + H_2O$

Properties : Unstable, weak acid

$3H\overset{+3}{N}O_2 \rightarrow H\overset{+5}{N}O_3 + H_2O + 2\overset{+2}{N}O$

$HNO_2 \xrightarrow[-H_2O]{} N_2O_3 \rightarrow NO + NO_2$

brown

HNO_2 salts – nitrites

$HNO_2 + NaOH \rightarrow NaNO_2 + H_2O$

sodium nitrite

HNO_2 – Good oxidising agent

Reduced to N_2O (or) NO and Oxidizes ~~reduces~~ H_2S to S

I^- to I_2

Fe^{+2} to Fe^{+3}

$H_2S + HNO_2 \rightarrow S + NO + H_2O$

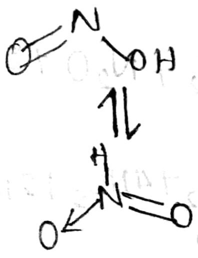
HNO_2 – Reducing agent oxidised to NO_3^-

$K_2Cr_2O_7$, $KMnO_4$, $Br_2 + H_2O$, H_2O_2, Cl_2, F_2

$HNO_2 + Br_2 + H_2O \rightarrow 2HBr + HNO_3$

$HNO_2 + H_2O_2 \rightarrow H_2O + HNO_3$

* *



Tautomeric structure

Nitric acid (HNO_3)

In Lab $NaNO_3$, KNO_3, NH_4NO_3

$$KNO_3 + H_2SO_4 \longrightarrow HNO_3 + KHSO_4$$

Birkland - Eyde process

1) $N_2 + O_2 \xrightarrow[\text{arc}]{\text{Electric}} 2NO \quad \Delta H = +180.9\ kJ/mole$

2) $2NO + O_2 \rightarrow 2NO_2$

3) $4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$

Ostwald's process

1) $4NH_3 + 5O_2 \xrightarrow[1273K]{Pt} 4NO + 6H_2O$

2) $2NO + O_2 \longrightarrow 2NO_2$

3) $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$

61% HNO_3

Step I - distillation - 68% HNO_3

Step II - con. H_2SO_4 - Azeotropic - 98% HNO_3

Step III - HNO_3 in freezing mixture - 100% pure

~~ph~~ properties: 1) HNO_3 is colourless liquid.

2) F.P - 231.4 K

3) B.P - 355.6 K

4) Good oxidising agent

$$4HNO_3 \xrightarrow{\Delta} 2NO_2 + 2H_2O + 3O_2$$

$$3M + \underset{(dil)}{8HNO_3} \longrightarrow 3M(NO_3)_2 + 2NO + 4H_2O$$

(M = Cu, Pb, Ag)

$$3Cu + \underset{(dil)}{8HNO_3} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$4Zn + \underset{(con)}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$M + 4\,con\,HNO_3 \longrightarrow M(NO_3)_2 + 4NO_2 + 2H_2O$$

M = Cu, Pb, Ag, Hg, Zn

$Cu + 4HNO_3 \text{ (conc)} \rightarrow Cu(NO_3)_2 + 4NO_2 + 2H_2O$

$Zn + 4HNO_3 \text{ (conc)} \rightarrow Zn(NO_3)_2 + 4NO_2 + 2H_2O$

$Sn + \text{dil. } HNO_3 \rightarrow Sn(NO_3)_2 + NH_4NO_3 + H_2O$

$NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$

$Sn + \text{con. } HNO_3 \rightarrow \underset{\text{Metastannic acid}}{H_2SnO_3} + NO_2 + H_2O$

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Cr, Ni, Al, Fe metals does not reacts with HNO_3 due to passivity (formation of oxide layer)

with non metals

$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 5H_2O$

$C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O$

$S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$

$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

Heating effect of nitrates

$2MNO_3 \xrightarrow{\Delta} 2MNO_2 + O_2$ (M = Na, K, Rb, Cs)

$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$

$2M(NO_3)_2 \xrightarrow{\Delta} 2MO + 4NO_2 + O_2$

(M = Ca, Mg, Sr, Ba, Ra)

$2M(NO_3)_2 \xrightarrow{\Delta} 2M + 4NO_2 + O_2$ (M = Ag, Au)

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

Aquaregia

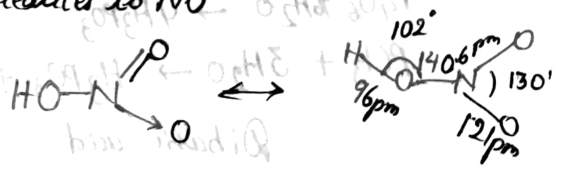
1 part HNO_3 + 3 part of HCl

$Au - H[AuCl_4]$ (or) $[AuCl_4]^- - Au^{+3}$

$Pt - [PtCl_6]^{-2} - Pt^{+4}$

NO_3^- reduces to NO

structure



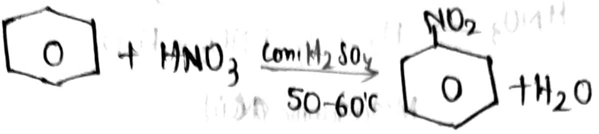
Uses: Basic calcium nitrate

→ TNT, nitroglycerine, explosives

→ perfumes, dyes

→ artifical silk – cellulose nitrate

→ con. HNO_3 + con. H_2SO_4 – nitration mixture



NO_3^- ion test

Brown Ring test

Salt soln + $FeSO_4$ + con. H_2SO_4

$3Fe^{+2} + NO_3^- + 4H^+ \longrightarrow 3Fe^{+3} + NO + 2H_2O$

$[Fe(H_2O)_6]^{+2} + NO \longrightarrow [Fe(H_2O)_5NO]^{+2} + H_2O$

Brown Ring complex

Oxoacids of phosphorous

two series of oxoacids

Q) When Zn reacts with dil. HNO_3

$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

amount of Zn required to required to 1mole of HNO_3 (at. wt of Zn 65.3)

4×65.3 $10NO_3^-$ $9NO_3^-$ only 1 reduced

$= 261.2g$ is required.

1) Phosphorous acid series

2) phosphoric acid series

I) Phosphorous acid series

1) orthophosphorous acid – H_3PO_3

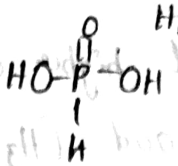
$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$ $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

Dibasic acid

two types of salts $H_2PO_3^-$ - primary phosphite

HPO_3^{-2} secondary phosphite



2 P–OH

1 P=O

1 P–H

OH^- group is responsible for basicity of acids & due P–H bonds it acts as good reducing agents.

$$H_3PO_3 + 2AgNO_3 + H_2O \rightarrow H_3PO_4 + 2Ag + 2HNO_3$$

2) Meta phosphorous acid (HPO_2)

HO–P=O basicity = 1

3) Hypophosphorous acid (H_3PO_2) (+1 oxidation of P)

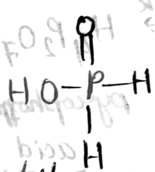
$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$ sodium hypophosphite

$\downarrow H^+$

H_3PO_2

Monobasic acid

Basicity = 1



1 P=O

1 P–OH

2 P–H

salts – hypophosphite

Action of heat

$$2\overset{+1}{H_3PO_2} \xrightarrow{\Delta} \overset{+5}{H_3PO_4} + \overset{-3}{PH_3}$$

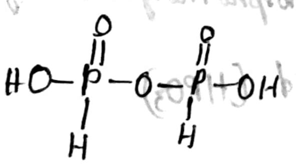
Good reducing agent

$$H_3PO_2 + 4AgNO_3 + 2H_2O \longrightarrow 4Ag + H_3PO_4 + 4HNO_3$$

$$H_3PO_2 + HgCl_2 + H_2O \longrightarrow Hg + H_3PO_4 + HCl$$

Pyrophosphorous acid ($H_4P_2O_5$) (P O. state +3)

$$2H_2O + PCl_3 + H_3PO_3 \longrightarrow H_4P_2O_5 + 3HCl$$



two P=O

two P–OH

two P–H

one P–O–P

Phosphoric acid series

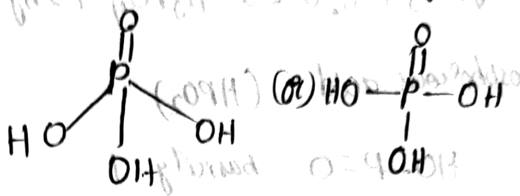
"P" exhibit higher O. state

1) Orthophosphoric acid (H_3PO_4) (+5 O.S)

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

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

→ Tribasic acid Basicity = 3



3 P-OH
1 P=O

→ 3 types of salts

$H_2PO_4^-$ – 1° phosphate (acidic) NaH_2PO_4

HPO_4^{-2} – 2° phosphate (acidic) Na_2HPO_4

PO_4^{-3} – 3° phosphate Na_3PO_4

$$H_3PO_4 \xrightarrow{520k} H_4P_2O_7 \xrightarrow[-H_2O]{870k} HPO_3$$

pyrophosphoric acid metaphosphoric acid

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

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Quantitative analysis

O.C → H_3PO_4
Organic compound

$$H_3PO_4 + 21HNO_3 + 12(NH_4)_2MoO_4$$

ammonium molybdate

$$\downarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$$

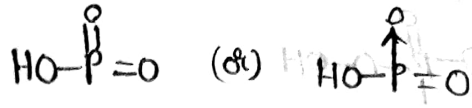
Ammonium phosphomolybdate (yellow)

Metaphosphoric acid (HPO_3)

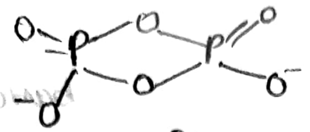
Glacial

$$H_3PO_4 \xrightarrow{520K} H_4P_2O_7 \xrightarrow{870k} HPO_3$$

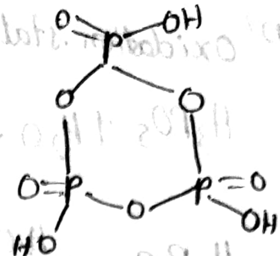
phosphorous acid + Br_2 heated in sealed tube HPO_3 is formed



Basicity = 1



Dimer



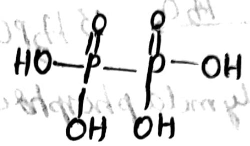
$(HPO_3)_3$

Trimer

Hypophosphoric acid ($H_4P_2O_6$)

Red P_4 + alkali $\longrightarrow$ $H_4P_2O_6$

$H_4P_2O_6$.



PO_4

q

Basicity = 4

'P' oxidation state = +4

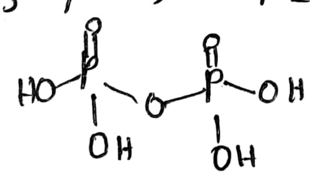
no of P–OH = 4

P=O = 2

Pyrophosphoric acid ($H_4P_2O_7$)

$H_3PO_4 + HPO_3 \xrightarrow{373K} H_4P_2O_7$

$H_3PO_4 \xrightarrow{520K} H_4P_2O_7$



Basicity = 4

o. state = +5

P–OH = 4

P=O = 2

P–O–P = 1

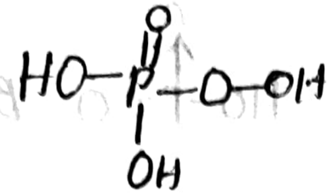
→ In these P is bonded at least one OH group

→ OH is responsible for basicity of acid

→ 'ous' acids consists of P–H bonds responsible for reducing property.

→ 'ic' acids does not contain P–H bonds.

(H_3PO_5) Peroxophosphoric acid



'P' oxidation state +5

basicity = 3

$$H_3PO_5 + H_2O \longrightarrow H_2O_2 + H_3PO_4$$

NOTE:

$$H_4P_2O_5 \xrightarrow{H_2O} 2H_3PO_3$$

$$H_4P_2O_6 \xrightarrow{H_2O} H_3PO_4 + H_3PO_3$$

$$H_4P_2O_7 \xrightarrow{H_2O} 3H_3PO_4$$

polymeta phosphoric acid