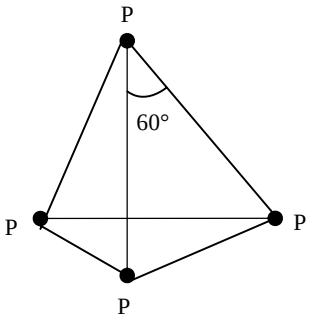
10. GROUP 15 ELEMENTS (V A GROUP ELEMENTS)

Synopsis :

- VA group elements are Nitrogen (N) (7), Phosphorus (P) (15), Arsenic (As) (33), Antimony (Sb) (51), Bismuth (Bi) (83).
- These elements are called as pnicogens.
- Their compounds are called pnictides.
- 78% of Atmosphere posses Nitrogen.
- It is also available in the form of nitrate salts in earth's crust.
  Eg : Salt petre KNO_3, Chile salt petre $NaNO_3$ etc,.
- Most abundant element of this group in earths crust is P.
- The important minerals of phosphorus are phosphate rocks, fluorapatite [$3Ca_3(PO_4)_2$, CaF_2], phosphorite [$Ca_3(PO_4)_2$] etc,.
- These are p–Block elements with $ns^2\,np^3$ configuration.
- As the P – orbitals in the outermost shells are half-filled these elements are stable.
- Nitrogen is a gas, P, As, Sb and Bi are solids.
- Nitrogen and Phosphorus are non – metals, Arsenic and antimony are metalloids and Bismuth is a metal.
- Nitrogen exists as triple bonded diatomic gaseous molecule. Bismuth is a metal (monoatomic).
- P, As and Sb exists as tetratomic, tetrahedral molecules.
- The existence of Nitrogen as diatomic molecule is due to existence of $p\pi$ - $P\pi$ multiple bonds.
- The bond dissociation energy of Nitrogen is 945.4kJ. (225 kcal/mole)
- $p\pi$ - $P\pi$ multiple bonds are not possible in other elements due to repulsion between non – bonded electrons of the inner core.
- Phosphorus form layered structures with a co-ordination number of 3.
- P_4 has a regular tetrahedral structure having one P atom at each vertex of the tetrahedron. The bond angle $\angle PPP$ is 60°.
- Atomic size increases from Nitrogen to Bismuth, less increase from As to Bi is because of less shielding effect of (n-1) d electrons.
- Due to smaller size of nitrogen it's electronegative value is high.
- Electronegativity decreases from nitrogen to Bismuth.
- B.P. increases from Nitrogen to Bismuth.
- M.P. increases from Nitrogen to Arsenic and then decreases.
- Low M.P of nitrogen is due to its diatomic discrete gaseous molecules.
- Due to large size and metallic character the M.P. of antimony and Bismuth decreases.
- Nitrogen in solid state exists in cubic crystalline structure (α - nitrogen) and hexagonal crystalline structure (β - nitrogen).
- Phosphorous exists in white, red, scarlet, violet, α - black, β - black etc. forms.
- Nitrogen can form a chain of two atoms (NH_2–NH_2) and a chain of three atom ($N_3^{(-)}$).
- Less catenation capacity for Nitrogen is due to less dissociation energy of N – N bond.
- Phosphorus forms (P_2H_4).
- The general oxidation states of these elements are +3 and +5 and –3 (except Bi).
- Stability of + 3 form increases from nitrogen to bismuth and + 5 decreases due to inert pair effect.

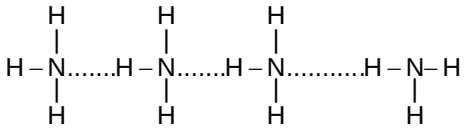


- Nitrogen show various oxidation states because of small size and high electronegativity. It shows
  – 3 in Li_3N, Mg_3N_2, Ca_3N_2 etc.
  – 2 in N_2H_4
  – 1 in NH_2OH
  $-\frac{1}{3}$ in N_3H
  0 in N_2
  + 1 in N_2O
  + 2 in NO
  + 3 in N_2O_3
  + 4 in NO_2
  + 5 in N_2O_5
- Phosphorous show – 3 in Zn_3P_2, Ca_3P_2.
- Nitrogen can show maximum covalency of 4 (NH_4^+).
- Remaining elements shows covalency of 5 and a maximum of 6 as in $AsF_6^{(-)}$, $PCl_6^{(-)}$.
- Phosphorous is reactive due to the presence of single P – P covalent bonds.

HYDRIDES :

- These elements form hydrides of the type MH_3
  NH_3(Ammonia) PH_3(Phosphine)
  AsH_3(Arsine) SbH_3(Stibine)
  BiH_3 (Bismuthine)
- NH_3 to BiH_3 the stability decreases.
- The size of the central atom increase and there by the metal – hydrogen bond becomes weaker due to decreased overlap between the large central atom and the small H – atom.
- Reducing character of these hydrides gradually increases. Stibine and bismuthine are strong reducing agents.
- All the hydrides can be prepared in similar methods. On hydrolysis of binary compounds of these metals with water or dilute acids gives these hydrides.
  $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 \downarrow + 2NH_3\uparrow$
  $Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3 \uparrow$
- NH_3 and PH_3 are volatile , colourless gases.
- The thermal stability of this hydrides decreases from $NH_3$to BiH_3 due to decrease in M – H bond energy.
- These hydrides have a pyramidal shape with a lone pair of electron on the central atom.
- In NH_3 N is sp^3 hybridised in other hydrides central atom uses pure p-orbitals.
- In NH_3 the bond angle is 107°.
- In PH_3 the bond angle is 94°.
- Due to presence of lone pair of electrons on the central atom these hydrides acts as lewis bases.
- The basic nature decreases as follows
  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
  Due to decrease in the electron density of the lone pair on the central atom.
  When Hydrogens are methylated basic nature increases $PH_3 < P(CH_3)_3$.
- Because of donation of lone pair of electron by NH_3 to H^+ ion NH_4^+ ion forms.
- Phosphonium (PH_4^+) ion is less stable.

- Due to high electronegative difference between Nitrogen and Hydrogen NH_3 is capable of forming hydrogen bonding.



- M–H bond energies $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

From NH_3 to BH_3 :

1) Thermal stability decreases
2) Reducing character increases
3) Basic nature decreases
4) Complex forming ability decreases
5) Ease of formation of hydrides decreases

HALIDES :

- All trihalides of these elements are possible except NBr_3 and NI_3 due to large size difference.
- Trihalides are covalent and have a tetrahedral structure.
- Trichlorides act as Lewis acids by utilizing the vacant d- orbitals.
- On hydrolysis of NCl_3 the products are NH_3 and HOCl.
- On hydrolysis of PCl_3 the main product is H_3PO_3 (Phosphorous acid).
- On hydrolysis of $ASCl_3$ the main product is H_3ASO_3 (Arsenious acid).
- On hydrolysis of $SbCl_3$ the main product is SbOCl (Antimony chloride).
- On hydrolysis of $BiCl_3$ the main product is BiOCl (Bismuthyl chloride).
  In SbOCl and BiOCl the radicals are SbO^+ and BiO^+ are present.
- With the increasing metallic character of the elements the halides become more ionic and their tendency towards hydrolysis decreases.
- PF_3 and PF_5 are not hydrolysed because P–F bonds are stronger bonds than P – O bonds.
- With the increase in the metallic character of the elements the halides become more ionic and their tendency towards hydrolysis decreases.
- All these elements except N and Bi doesn't form pentahalides. N because of non – available vacant d –orbitals and Bi due to inert pair effect.
- PCI_5 and $SbCl_5$ exists in triagonal bipyramid structures.
- But as some bond angles are 90° and some are of 120° they are not stable.
  $PCl_5 \Leftrightarrow PCl_3 + Cl_2$(chlorinating agent)
- Hydrolysis of PCl_5 gives orthophosphoric acid.
  $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$
- Solid PCl_5 is ionic compound consisting of $[PCl_4]^+$, $[PCl_6^{(-)}]$ cation is tetrahedral anion is octahedral.
- PBr_5 exists as $[PBr_2]\ Br_3^{(-)}$.

OXIDES :

Oxides of Nitrogen :

- Oxides of N_2 are endothermic (except N_2O_5) and acts as better oxidants.
- Except N_2O_5 all are gases.
- **N_2O (Laughing gas)**: First prepared by priestly.
- Berthelot prepared it from Ammonium nitrate or ammonium sulphate and sodium nitrate.

$$NH_4NO_3 \xrightarrow{250^0C} N_2O + 2H_2O$$

$(NH_4)_2SO_4 + 2NaNO_3 \rightarrow N_2O + H_2O + Na_2SO_4$

- It is colourless neutral gas.
- Fairly soluble in cold water.
- It is incombustible but supports combustion of Mg and P.

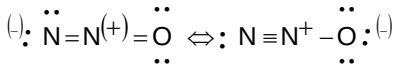
  $Mg + N_2O \rightarrow MgO + N_2$

  $P_4 + 10\ N_2O \rightarrow P_4O_{10} + 10N_2$
- Oxidising property : - It oxidises metals.

  $Cu_{(hot)} + N_2O \rightarrow CuO + N_2$
- Mixture of O_2 and N_2O is used as anaestheic in surgery and dentistry.
- In the presence of acidified potassium permanganate it undergoes oxidation to give nitric oxide.

$2KMnO_4 + 3H_2SO_4 + 5N_2O \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 10NO$

- **Structure :** N_2O is hybrid of following structures. It is a linear molecule.



Nitric oxide (NO) Nitrogen monoxide : (Priestley)

1) $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

2) Catalytic oxidation of Ammonia gives Nitric oxide. (Ostward's method) .

$$4NH_3 + 5O_2 \xrightarrow[900^0C\ 600m]{pt\ gauze} 4NO + 6H_2O$$

3) By passing electric arc through N_2 and O_2

$N_2 + O_2 \rightarrow 2NO$

Properties :

- NO is colourless gas and heavier than air.
- At 12 K it freezes to Blue solid & its M.P is 1232 K.
- On reaction with oxygen it gives reddish brown fumes.

  $2NO + O_2 \rightarrow 2NO_2$
- NO is most thermally stable oxide of N_2.

$$2NO \xrightarrow{900^0C} N_2 + O_2$$

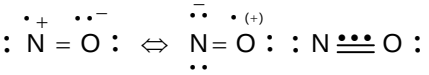
- Oxidising properties :

  $H_2S + 2NO \rightarrow H_2O + N_2O + S$

  $2Cu + 2NO \rightarrow 2CuO + N_2$
- In the manufacture of H_2SO_4 by lead chamber process NO is used as catalyst.

  Structure : NO has 11 valence electrons

  (N$\rightarrow$ 5, O $\rightarrow$ 6).
- Presence of odd, electron makes it as paramagnetic.
- It doesn't dimerises due to delocalised odd electron.



- In liquid and solid states it dimerises hence it is diamagnetic.

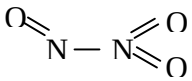
Nitrogen sesquioxide or dinitrogen trioxide (N_2O_3) :

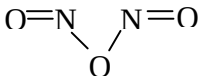
- N_2O_3 is a hydride of nitrous acid.

  $N_2O_3 + H_2O \rightarrow 2HNO_2$

- By cooling a mixture of NO and NO_2 in equimolar ratio to – 20°C N_2O_3 is obtained.
  $NO + NO_2 \Leftrightarrow N_2O_3$
- On action of Cu on HNO_3 N_2O_3 is obtained.
  $2Cu + 6HNO_3 \rightarrow N_2O_3 + 2Cu(NO_3)_2 + 3H_2O$
- It is blue liquid and a pale blue solid.
- M.P is –102° C.
- It is acidic oxide.
- It's salts are called as nitrites.
  $2NO + 2KOH \rightarrow KNO_2 + H_2O$

Structure :

i) 

ii) 

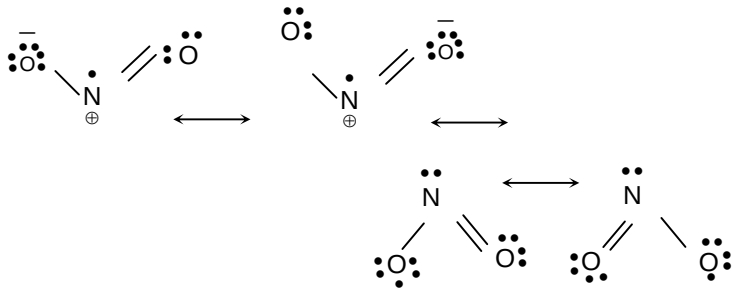
Nitrogen Dioxide :

- It is reddish brown gas.
- It dimerises to dinitrogen tetraoxide which is colourless solid.

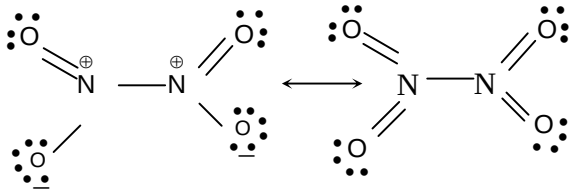
$$\underset{\text{Brown Paramagnetic}}{2NO_2} \xrightarrow{-11^0C} \underset{\text{Colourless solid diamagnetic}}{N_2O_4}$$

- Reduction of conc nitric acid with metals like Cu, Ag gives NO_2.
  $Cu + 4HNO_3 \rightarrow 2CuO + 4NO_2 + O_2$
- Lead nitrate on heating gives NO_2
  $Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$
- NO_2 dissolves in water to give nitrous and nitric acids hence it is called as mixed anhydride of HNO_2 and HNO_3.
  $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

Structure : NO_2 has angular structure with a bond angle of 132° . It posses a three electron bond and hence it is coloured and paramagnetic.



The structure of N_2O_4 :



- It turns ferrous sulphate solution black.
- NO_2 gives nascent oxygen hence it acts as oxidizing agent $NO_2 \rightarrow NO + (O)$

  $SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO$

  $H_2S + NO_2 \rightarrow S + NO + H_2O$
- When reacts with alkalis it form nitrates and nitrites.

  $2NO_2 + 2KOH \rightarrow KNO_2 + KNO_3 + H_2O$

Nitrogen pentaoxide :

- On dehydration of Nitric acid with the help of phosphorous pentoxide N_2O_5 is obtained.

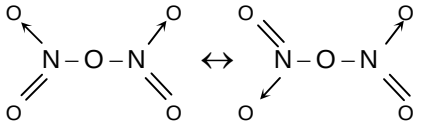
  $2HNO_3 \xrightarrow{P_4O_{10}} N_2O_5 + H_2O$
- $4AgNO_3 + 2Cl_2 \rightarrow 4AgCl + 2N_2O_5 + O_2$
- N_2O_5 is white solid.
- M.P. 35°C.
- Above it's melting point it decomposes to N_2O_4 and O_2 .

  $2N_2O_5 + H_2O \rightarrow 2HNO_3$
- It is anhydride of nitric acid.

  $N_2O_5 + H_2O \rightarrow 2HNO_3$
- It reacts with bases to give nitrate salts.

  $N_2O_5 + 2NaOH \rightarrow 2NaNO_3 + H_2O$
- As it decomposes easily it acts as powerful oxidizing agent.

  Structure :
- It is an ionic solid i.e, Nitronium nitrate (NO_2^+,NO_3^-)

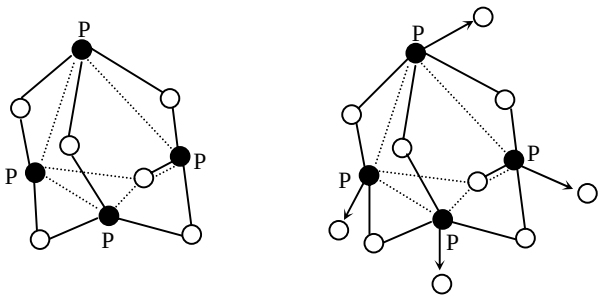


- As the size of the central atom increases the basic property increases.
- Phosphorous forms the following oxides.

+3	+4	+5
P_2O_3	P_2O_4	P_2O_5

- P_2O_3 and P_2O_5 exist as dimmers P_4O_6 and P_4O_{10}.

P_4O_6 **P_4O_{10}**



Phosphorus is linked to 3 oxygens

Phosphorus is linked to 4 oxygens

- Acidic character of the oxides increases with increases in the oxidation state of central atom.
- Oxides of Nitrogen and phosphorous are acidic. As and Sb are amphoteric and Bismuth are basic.

OXYACIDS OF NITROGEN :

Hypo nitrous acid : HNO (or) $H_2N_2O_2$:

The molecular formula of Hypo nitrous acid is $H_2N_2O_2$

Nitrous acid (HNO_2) :

Nitrous acid is unstable except in dilute solutions

In the laboratory it is prepared by the addition of ice cold dilute acid to Barium nitrite

$$Ba(NO_2)_2 + \underset{(\text{ice cold})}{H_2SO_4} \rightarrow BaSO_4 + 2HNO_2$$

Its solution is slightly bluish in colour due to the presence N_2O_3.

On standing it undergoes auto oxidation-reduction in acidic solution

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

In this reaction

In $HNO_2 \rightarrow HNO_3$ O.S of 'N' changes from +3 to +5

In $HNO_2 \rightarrow NO$ O.S of N changes from +3 to +2

i.e "HNO_2" as oxidant changes to 'NO' and as reductant changes to "HNO_3"

With oxidising agents stronger than HNO_2 like $KMnO_4$, $K_2Cr_2O_7$, $Br_2 + H_2O$ or H_2O_2 solutions HNO_2 functions as reductant.

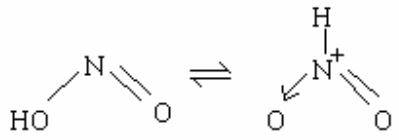
Where as with weaker oxidants i.e reducing agents like H_2S, SO_2 'or' Sn^{+2} solutions HNO_2 functions as oxidant

At low temperatures HNO_2 reacts with aromatic primary amines and gives "diazonium compounds"

Diazonium compounds can be converted into different substituted aromatic compounds

Structure of (HNO_2) :

HNO_2 exists in two tautomeric forms i.e in two structural isomers.



Tautomers and resonance hybrids :

In Tautomers the skeleton of atoms in the structures differs

In resonance hybrids the skeleton of atoms doesn't change

HNO_2 is a weak acid and its salts are known as nitrites

Ex : Sodium Nitrite $NaNO_2$

It is obtained by dissolving N_2O_3 in water.

It is an unstable and weak acid.

It acts as an oxidising and reducing agent.

Its structure is HO - N = O

Nitric acid (HNO_3) : "Aqua fortis"

In laboratory it is prepared by the action of conc H_2SO_4 on KNO_3 or NH_4NO_3

$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3$

A mixture of 1 : 1 conc HNO_3 and Conc H_2SO_4 is known as nitration mixture

It is used in nitration reaction of organic compounds like Benzene, Toluene and phenol

$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$

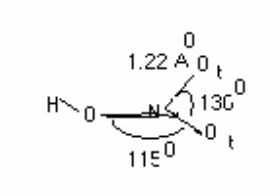
It is a very strong oxidising agent. It oxides non-metals to their corresponding oxides or oxoacids

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

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

The structure of nitric acid is

$$HO-\underset{\downarrow}{\underset{O}{N}}=O \rightleftharpoons HO-\underset{\|}{\underset{O}{N}}\rightarrow O$$

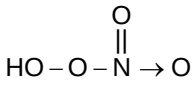


This is a monobasic acid

It is a strong oxidising agent

Pernitric acid :

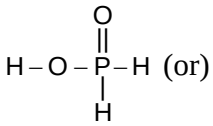
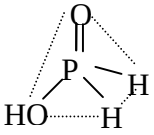
- HNO_4 is called as per nitric acid.



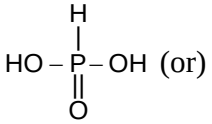
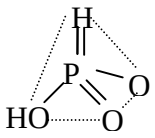
Oxyacids of phosphorous :

- **Hypophosphorous acid : (H_3PO_2)**
- Salts are called as hypophosphates.
- It decomposes on heating to give PH_3.
- The acid and its salts are powerful reducing agents.
- Basicity of H_3PO_2 is one.

Structure :


(or)


- **Ortho Phosphorous acid : (H_3PO_3)**
- Forms two series of salts phosphite (Normal) and hydrogen phosphite (Acidic).
- Decomposes on heating to give PH_3 and H_3PO_4.
- It gives two series of salts primary phosphites (H_2PO_3) and secondary phosphites (HPO_3^{-2}).
- H_3PO_4 and its salts are good reducing agents.
- Structure :


(or)


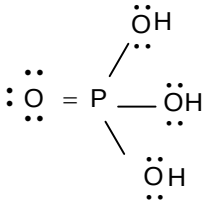
- **Orthophosphoric acid (H_3PO_4) :**

- $Ca_3(PO_4)$ with H_2SO_4 gives H_3PO_4.
- P_2O_5 on hydrolysis gives H_3PO_4.
- Forms three types of salts (basicity is three).
  Dihydrogen phosphate $\left(H_2PO_4^-\right)$.
  Hydrogen phosphate $\left(HPO_4^{2-}\right)$.
  Phosphate $\left(PO_4^{3-}\right)$.
- It is syrupy liquid due to hydrogen bonding.
- The acid looses water steadily on heating.

$$H_3PO_4 \xrightarrow{\text{gently heating}} H_4P_2O_7 \xrightarrow{\text{strong heating}} HPO_3$$

(orthophosphoric acid) (pyrophosphoric acid) (meta phosphoric acid)

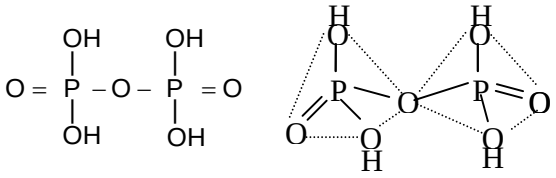
Structure :



- Used in the preparation of HBr and HI.

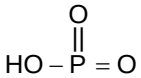
Pyrophosphoric acid : ($H_4P_2O_7$) :

- It forms salts of type $M_4P_2O_7$ and $M_2H_2P_2O_7$.
- $Ca_2P_2O_7$ is used in fluoride tooth pastes.
- $Na_2H_2P_2O_7$ is used in making bread.
- It is a Tetrabasic acid.
  Structure :



Metaphosphoric acid (HPO_3) :

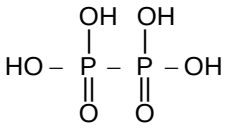
- By heating H_3PO_4 or $H_4P_2O_7$ it is obtained.
- As it is transparent, glassy solid it is known as glacial phosphoric acid.
- It's salts are known as metaphosphates .
- Free monophosphate (PO_3^-) ions doesn't exist where as it forms a ring compounds like triphosphates, tetraphosphates or polyphosphates.
- It's polymeric sodium metaphosphates are called as Graham's salt , Kurrol's salt and madrell's salt $(NaPO_3)_n$.
- It is a monobasic acid.
  Structure :

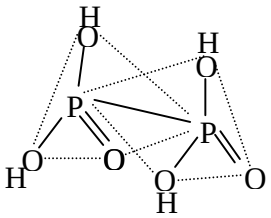


Hypophosphoric acid ($H_4P_2O_6$) :

It is a tetrabasic acid.

Structure :

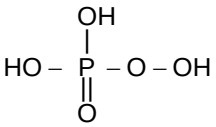




Peroxy phosphoric acid(H_3PO_5) :

It is a Tribasic acid.

Structure :



PREPARATION AND USES OF NITRIC ACID : (HNO_3)

HNO_3 is the most important oxy acid of Nitrogen

HNO_3 is prepared on large scale by

1) Birkland-Eydes process (Arc process)

2) Ostwald's process (from ammonia)

- **BIRK LAND-EYDES PROCESS** used at places where electric power is cheap.

PRINCIPLE:-

$$N_2 + O_2 \xrightarrow{Electric\ arc} 2NO;\ \Delta H = +180.7kJ$$

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

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

- **OSTWALD'S PROCESS (FROM AMMONIA) :**

NH_3 mixed with air in 1 : 7 or 1 : 8 when passed over a hot platinum gauze catalyst is oxidised (95%) to NO

$$4NH_3 + 5O_2 \xrightarrow[1155K]{pt\ gauze} 4NO + 6H_2O + 1275\ K.J$$

- The liberated heat keeps the catalyst hot

The NO gas is cooled and mixed with oxygen to get NO_2 in oxidation chamber.

Then it is passed into warm water under pressure in presence of excess air where HNO_3 is formed.

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

The acid formed is about 61% concentrated.

Concentration of HNO_3 :

The crude HNO_3 is concentrated in three stages

Stage-1 61% HNO_3 is distilled until 68% HNO_3 is obtained

Stage-2 68% HNO_3 is mixed with Conc H_2SO_4 and distilled again where 98% acid is obtained.

Stage-3 98% HNO_3 is cooled in a freezing mixture then crystals of pure HNO_3 seperates out.

Uses of HNO_3 :

- In the manufacture of fertilisers like basic calcium nitrate [$CaO.Ca(NO_3)_2$]
- In the preparation of explosives like TNT, nitroglycerine etc.

as nitration mixture along with H_2SO_4

- In the preparation of perfumes, dyes and medicines
- HNO_3 is a very strong oxidising agent used in the oxidation of cyclohexanol or Cyclohexanone to adipic acid, p-xylene to terepthalic acid
- In the preparation of artificial silk i.e "cellulose nitrate"

Ammonia :

- Distillation of NH_4^+ salt with a base gives ammonia.

$NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$

Cyanamide process :

- Calcium carbide on reaction with nitrogen gas at 1273k in the presence of $CaCl_2$ or CaF_2 as catalyst gives calcium cyanamide and graphite mixture. This is called as nitrolim.

$$CaC_2 + N_2 \xrightarrow{1273-1378K} CaCN_2 + C$$

- Hydrolysis of cyanamide with steam gives NH_3.

$$CaCN_2 + 3H_2O \xrightarrow{453K} CaCO_3 + 2NH_3$$

Haber – Bosch process :

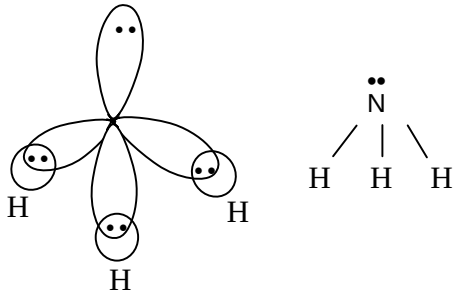
- H_2 and N_2 gives in 3 : 1 ratio with iron as catalyst and Mo or small amounts of mixture of potassium and aluminium oxides (K_2O and Al_2O_3) as promoter and at a pressure of 200 atm, 725 – 775 k. gives ammonia.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = -93.63$ kJ

- In serpeck's process by product is NH_3.
- Quick lime is used to dry NH_3.
- $CaCl_2$, P_2O_5 and H_2SO_4 are acidic hence they can't be used as drying agents for NH_3.
- At 20°C 1 litre H_2O dissolves 700 litres of NH_3.
- Saturated sol of NH_3 at room temperature contains 35% (w/w) NH_3.
- NH_3 in the presence of catalyst gives NO.
- NH_3 with hot CuO gives N_2 gas.
- With lesser Cl_2 on oxidation NH_3 gives N_2 and with excess Cl_2 gives NCl_3.
- NH_3 is Lewis base.
- NH_3 acts as ligand and forms complexes like $[Ag(NH_3)_2]^+$, $[Cu(NH_3)_4]^{2+}$ etc.

Uses of Ammonia :

- NH_3 is used in refrigeration due to high latent heat of evaporation.
- For nitrogenous fertilizers like ammonium sulphate, urea, calcium ammonium nitrate etc. Preparation, ammonia is the starting material.
- In the manufacture of sodium carbonate by Solvay process ammonia is used.
- In the preparation of rayon and artificial silks, explosive like ammonium nitrate, ammonia is required.
- Nitric acid manufacture (by Ostwarld's process), explosive like ammonium nitrate, ammonia is required.
- Liquior ammonia is useful as a good solvent for both ionic as well as covalent compounds.
- Structure : Pyramidal in shape, Hybridisation sp^3.



- A mixture of CaC_2 + Ca_3 P_2 is used as Holmes signals.
- **Superphosphate of lime (calcium superphosphate) $Ca(H_2PO_4)_2$ + 2($CaSO_4$ .2H_2O)**
- Mixture of calcium dihydrogen phosphoate [$Ca(H_2PO_4)_2$] and gypsum ($CaSO_4.2H_2O$) is known as super phosphate of lime.
- Powdered phosphate rock (calcium phosphate) on treating with concentrated sulphuric acid (chamber acid)

  $Ca_3(PO_4)_2+2H_2SO_4+4H_2O\rightarrow$

  $Ca(H_2PO_4)_2+ 2(CaSO_4. 2H_2O)$ + heat
- The reaction between phosphate rock and conc. H_2SO_4 is allowed to take place for 24 – 36 hours.
- In the above reaction the temperature rises to about 373 – 383 K.
- The carbonate and the fluoride impurities in the phosphate rock react with H_2SO_4 and liberate CO_2 and HF gases.
- **Uses:** Superphosphate of lime is a good phosphate fertilizer.
- $CaSO_4$ present in superphosphate of lime is insoluble waste product. To avoid it superphosphate is changed into triple phosphate which is completely dissolves in water.