

p-BLOCK ELEMENTS

Preface

This booklet is designed not only to reinforce the students formal knowledge about "**p-Block Elements**" but also complete coverage of non-metals families. The main objective behind putting up prudently organised strategic edition of this booklet is to develop their urge to excel & ability for original thinking, to offer them the unique joy that only solving of truly challenging problem can bring, to acquiring them with chemical ingenuity & idea which is new to them.

We have meticulously culled out the latest & the most relevant mechanism aspects of reaction & the latest challenging problems.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develop better understanding of the chapter and to have better grasping level in the class.

Total number of Questions in p-Block Elements are :	
In Chapter Examples	00
Solved Examples	23
Total no. of questions	23

NITROGEN FAMILY

1. NAMING ::

Commonly Called as Pnicogens and their Compounds are Pnictides :

2. ELECTRONIC CONFIGURATION ::

N	7
P	15
As	33
Sb	51
Bi	83

ns^2np^3

3. IMPORTANT POINT ::

Hydrides of these elements are very poisonous and on their presence breathing is difficult

4. GENERAL PROPERTIES ::

4.1 State and Nature :

- Only N is gaseous and rest are all solids.
- N and P are both non metallic.
- As is metalloids.
- Sb and Bi are metal.
- The existence of Nitrogen as diatomic molecule is due to its ability to form $p\pi - p\pi$ multiple bonds which is not possible in case of other elements.

4.2 Atomic Radius, Density, Ionic Radius and M.P.:

↓ increases due to Electro positive character increases.

4.3 Ionisation Energy and Electronegativity :

I.P. and E.N. ↓ Decreases.

4.4 Electrical and Thermal Conductivity :

↓ Increases.

Because delocalisation of electron increases. from N to Bi.

∴ N, P As Sb, Bi
 Poor conductor Semi conductor Good conductor

4.5 Catenation :

Only N, P and As exhibit the property of catenation.

4.6 Valency and Oxidation Number :

- (a) Gen. configuration : $ns^2 \quad np^3$
 Valency = 3
 O.S. = - 3, + 3, + 5
 P show O.S. = - 3, + 3

(b) P has two sleeping valency.

(c) **Sleeping Valency** : These e^- of valency shell which does not take part in bonding.

(d) P in E.S. show + 5 O.S.

So Hybridisation = sp^3d

Shape = Triagonal bipyramidal.

(e) P, As, Sb Show 3 & 5 both O.S.
 N only 3 absence of
 d - orbital

Bi only 3 because of inert pair effect

4.7 Reactivity :

- ↓ Decreases ∴ E.N. Decrease
- Least reactive in V group is N {due to triple bond formation of Bond Energy (↑)}
- Max. reactive in V group is P.
- Order $P > As > Sb > Bi > N$

4.8 Allotropic Forms :

- N in solid state has α and β allotropy
- [Liquid N + liquid HNO_2] → employed for surgery called cryo surgery. It is painful surgery without surgical instruments.

5. TYPES OF PHOSPHOROUS ::

- Yellow or white Phosphorous
- Red Phosphorous
- Black Phosphorous

5.1 White P :

- White P exist as discrete P_4 molecules. It has tetrahedral geometry. Bond angle is 60° instead of 109° . With this Bond angle white P is associated with strain and because it is less stable or more reactive.

: Properties of Hydrides :

S.No.	Property	NH ₃	PH ₃	AsH ₃	SbH ₃	BiH ₃
1.	Physical State	Gas	Gas	Gas	Gas	Gas
2.	Smell	Specific	Rotten Fishy	Garlic Odour	Unpleasant	Unpleasant
3.	Solubility	Very Soluble	Sparingly Soluble	Insoluble	Insoluble	Insoluble
4.	Stability	Very High	High	Low	Very Low	Unstable
5.	Bond Angle	106.5°	93.3°	91.8°	91.3°	Unstable
6.	Nature	Non Poisonous	Poisonous	Poisonous	Poisonous	Poisonous

6.2 Formation of Halides :

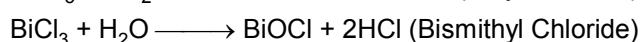
- (i) YX₃ (ii) YX₅

(i) Tri Halides :

All possible trihalides of all these elements are known except NCl₃, NBr₃, and NI₃

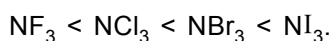
Because :

- (1) Low polarity of the N – X bond.
- (2) Weakness of N – X bond due to large size difference.
- (3) NCl₃ + 3H₂O → NH₃ + 3HOCl
 PCl₃ + 3H₂O → H₃PO₃ + 3HCl



When an aq. solution of BiCl₃ is prepared after some time a turbidity appears which is milky in appearance and finally a white ppt is formed due to formation of BiOCl.

- (4) Lewis Base Order :



(ii) Penta Halides :

- (1) Except N and Bi all forms pentahalides N does not form due to absence of d-orbital Bi does not form due to inert pair effect.
- (2) PCl₅ acts as an effective chlorinating Agent so it decomposes into
 PCl₅ → PCl₃ + Cl₂

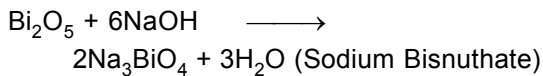
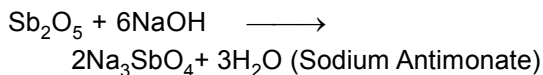
6.3 Formation of Oxides :

- (i) N₂O : laughing Gas
Highly poisonous gas, in very little amount it will have hysteric effect.
- (ii) N ≡ N → O It has linear geometry μ must be zero but it is more than zero because it has only one polar bond.
- (iii) Only NO and N₂O are neutral oxides of N.
- (iv) It is only N which forms paramagnetic oxide.
- (v) Stability of oxides decreases with increasing atomic number.
Eg. Thus N₂O₅ is stable while Bi₂O₅ is not known.
- (vi) The Acidic Character of Oxides Decrease with decrease in O.S.
Eg. N₂O +1 ⇒ Neutral
While NO₂ +4 ⇒ Acidic

(vii) Types of Oxides :

Element Types of Oxides	N	P	As	Sb	Bi
X ₂ O ₃	N ₂ O ₃	P ₂ O ₃	As ₂ O ₃	Sb ₂ O ₃	Bi ₂ O ₃
X ₂ O ₄	N ₂ O ₄	P ₂ O ₄	As ₂ O ₄	Sb ₂ O ₄	Bi ₂ O ₄
X ₂ O ₅	N ₂ O ₅	P ₂ O ₅	As ₂ O ₅	Sb ₂ O ₅	

(viii) Sb_2O_5 and Bi_2O_5 are insoluble in water but dissolve in alkali.



Exception : P_2O_5

7. ABNORMAL BEHAVIOUR OF NITROGEN ::

- Nitrogen is a gas, while other elements are solids.
- Nitrogen molecule is diatomic (N_2) while molecules of P, As and Sb are tetra atomic (P_4 , As_4 , Sb_4) and that of Bi is mono atomic.
- Halides of nitrogen except NF_3 are highly explosive.
- N_2O_3 and N_2O_5 are monomeric while trioxides and pentoxides of P, As and Sb are dimeric.
- It is chemically inert due to the presence of triple bond other elements are highly reactive due to presence of single bond in their molecule.
- $\text{N} \equiv \text{N}$, $\text{C} = \text{O}$, $(\text{C} \equiv \text{N})^-$ are isoelectronic species but $\text{N} \equiv \text{N}$ is less reactive due to nonpolar nature and high ionisation energy.
- N does not form sulphides.
- Nitrogen occurs in free state but others are not.

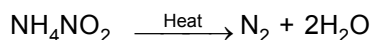
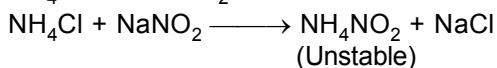
8. FAMILY MEMBERS OF V-A GROUP ::

8.1 Nitrogen (N_2) :

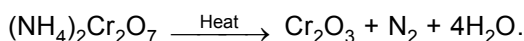
(1) N_2 forms 75% by mass or 78% by volume of the air.

(2) Preparation :

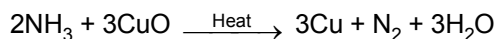
(i) Lab Method : By heating a mixture of NH_4Cl and NaNO_2 .



(ii) By heating ammonium dichromate :



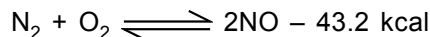
(iii) By oxidation of Ammonia



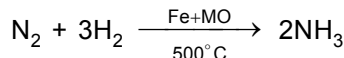
(iv) Commercially nitrogen is obtained by liquefaction of air. The resultant liquid is fractionally distilled in Claude's apparatus.

(3) Properties :

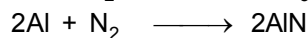
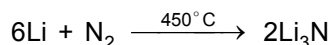
(i) Combination with oxygen to form NO (Nitric oxide) i.e. (Birkeland and Eyde Process) :



(ii) Reaction with hydrogen (Haber's process)



(iii) Reaction with metals :

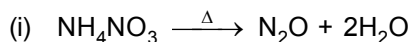


(iv) $\text{CaC}_2 + \text{N}_2 \xrightarrow{1000^\circ\text{C}} \text{CaCN}_2$ (Calcium Cyanide Nitrolium)

8.2 Compounds of Nitrogen

8.2.1 Oxides :

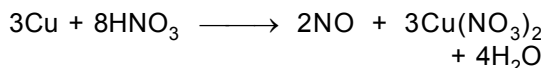
(a) Nitrous oxide or laughing Gas (N_2O) :



It is poisonous and when inhaled in small quantities it causes hysterical laughing.

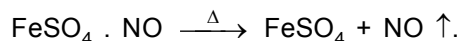
(b) Nitric oxide (NO) :

(i) By the action of dil. HNO_3 on Cu : (Lab Method)



(ii) This is the only gas which gives coloured gas on reaction with O_2 (Blue colour.)

(iii) FeSO_4 is employed for purification of NO.

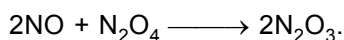


(iv) On lowering the temperature paramagnetic nature of NO decreases and in the liquid state it becomes diamagnetic in nature.

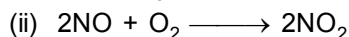
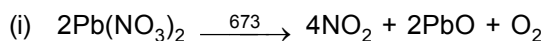
(v) $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ (Reddish brown fume)

(vi) $2\text{NO} + \text{Cl}_2 \longrightarrow 2\text{NOCl}$

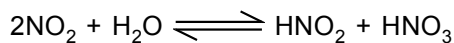
(c) Dinitrogen Trioxide : (N_2O_3)



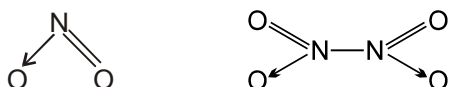
(d) Nitrogen Dioxide (NO_2) :



- (iii) It is a reddish brown gas.
 (iv) It is a mixed anhydride of Nitrous and Nitric acids.



- (v) $2\text{NO}_2 \xrightarrow{-110^\circ\text{C}} \text{N}_2\text{O}_4$
 Reddish Brown Colourless
 (Unpaired electron) (Dimagnetic)
 NO₂ molecule is paramagnetic and V shaped but dinitrogen tetroxide molecule is diamagnetic and have long N – N bond in its structure and hence weak.



Nitrogen dioxide Dinitrogen Tetraoxide

(e) Nitrogen Penta oxide or Nitric Anhydride (N₂O₅) :

- (i) It is prepared by dehydration of HNO₃ and P₂O₅
 $2\text{HNO}_3 + \text{P}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$
 (ii) It is a white crystalline solid but it becomes yellow due to partial decomposition into NO₂.
 $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$
 (iii) It is Anhydride of Nitric Acid
 $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_3$.
 (iv) It is also called Nitronium (NO₂⁺) nitrate (NO₃⁻).

8.2.2 Oxy acids of Nitrogen :

- (1) Nitrous Acid : HNO₂
- (2) Nitric Acid : HNO₃
- (3) Per Nitrous Acid : HOONO
- (4) Per Nitric Acid : HNO₄
- (5) Hypo Nitrous Acid : H₂N₂O₂.

But two are mains

(1) Nitrous Acid (HNO₂) :

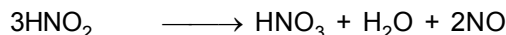
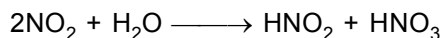
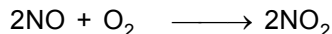
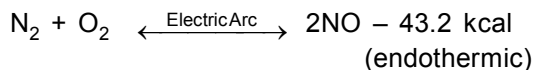
- (i) It is used in Mfg. of azo - dyes.
- (ii) HNO₂ is very unstable and exists only in aq. solution

(2) Nitric Acid (HNO₃) :

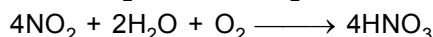
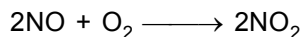
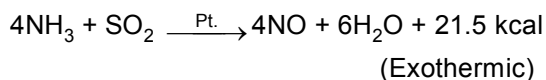
- (i) Commonly called as **Aqua Fortis**. This indicates that strong water, when it falls on skin it causes mild burning.
- (ii) N is in sp² hybridisation in HNO₃ and shape is trigonal planar geometry.

8.2.3 Preparation :

A. Birkland and Eyde Process :



B. Ostwald Process :



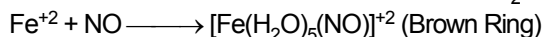
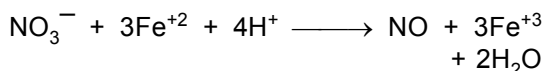
- * Conc. increased up to 98% by dehydration with conc. H₂SO₄.

8.2.4 Properties of HNO₃ :

- (i) Action on gold and platinum : These metals do not react even with hot and conc. HNO₃. However these dissolve in Aqua regia (a mixture of 3 parts of conc. HCl and one part of conc. HNO₃).
 $3\text{HCl} + \text{HNO}_3 \longrightarrow \text{NOCl} + 2\text{H}_2\text{O} + 2[\text{Cl}]$
 $\text{Au} + 3[\text{Cl}] \longrightarrow \text{AuCl}_3 \xrightarrow{\text{HCl}} \text{HAuCl}_4$
 (Aurochloric acid)
 $\text{Pt} + 4[\text{Cl}] \longrightarrow \text{PtCl}_4 \xrightarrow{2\text{HCl}} \text{H}_2\text{PtCl}_6$.
- (ii) Reaction with copper :
 $\text{Cu} + 4\text{HNO}_3 (\text{conc.}) \longrightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
 $3\text{Cu} + 8\text{HNO}_3 (\text{dil.}) \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
- (iii) Reaction with zinc :
 $4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$
 While $4\text{Zn} + 10\text{HNO}_3 (\text{dil.}) \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NH}_3 + 3\text{H}_2\text{O}$
- (iv) Reaction with non metals :
 (a) $\text{I} + 10\text{HNO}_3 \longrightarrow \text{HIO}_3 (\text{Iodic Acid}) + 10\text{NO}_2 + 4\text{H}_2\text{O}$
 (b) $\text{C} + 4\text{HNO}_3 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{NO}_2$
 (c) $\frac{1}{8}\text{S}_8 + 6\text{HNO}_3 (\text{conc.}) \longrightarrow \text{H}_2\text{SO}_4 + 6\text{NO}_2 + 2\text{H}_2\text{O}$
 (d) $\text{P}_4 + 20\text{HNO}_3 (\text{conc.}) \longrightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$

8.2.5 Brown Ring Test :

Brown ring test for nitrates depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide which reacts with Fe^{2+} to form a brown coloured complex. The test is usually carried out by adding dilute ferrous sulphate to an aqueous solution suspected of containing nitrate ion, and then carefully adding concentrated sulphuric acid through the sides of the test tube so that a separate layer is formed.



- Uses :** (a) Preparation of explosive such as T.N.T, Picric acid, Gun cotton and dynamite.
(b) In purification of Ag and Au.

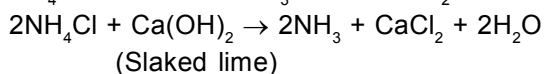
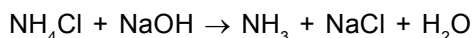
8.3 Family members

8.3.1 Ammonia (NH_3) :

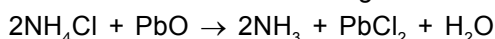
Discovery : - Berthelot, in 1788, pointed out that ammonia is a compound of nitrogen and hydrogen. In 1800, Davy established its formula NH_3 .

Preparation: -

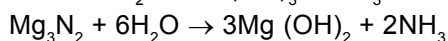
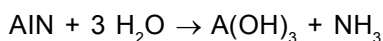
- (i) Ammonia is obtained on a small scale from ammonium salts which evolve it when heated with caustic soda or lime.



- (ii) Ammonia is formed when ammonium chloride is heated with litharge

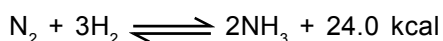


- (iii) By reacting nitrides with water, ammonia is obtained.



Manufacture of Ammonia

- (i) **Haber's process : Principle :** Haber process is the most important industrial method of preparing ammonia. This method was discovered by a German chemist Fritz Haber. The method involves the direct combination of nitrogen and hydrogen according to the following reaction.



The reaction is reversible, exothermic

and formation of NH_3 is followed by a decreased in volume. According to Le Chatelier's principle, the optimum conditions for the greater yield of ammonia are :

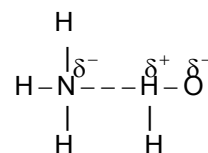
- (a) **High pressure :** Usually a pressure of 200 atmospheres is applied.
(b) **Low temperature :** The working temperature of $450\text{--}550^\circ\text{C}$ is maintained.
(c) **Catalyst :** At low temperature, although the yield of ammonia is more yet the reaction is very slow. In order to speed up the reaction, a catalyst is used. The following catalysts have been proposed for this purpose.
(i) Finely divided iron with some molybdenum as a promotor.
(ii) Finely divided nickel and sodalime deposited over pumice stone.

Raw materials : Nitrogen and hydrogen are the chief raw materials. Nitrogen is obtained from air by liquefaction followed by fractional evaporation of liquid air. Hydrogen is obtained by electrolysis of water.

Physical properties : (i) Ammonia is a colourless gas with a characteristic pungent odour. It brings tears into the eyes.

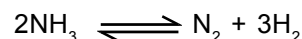
- (ii) It is lighter than air .

- (iii) It is highly soluble in water. One volume of water dissolves 1300 volume of ammonia at 0°C and 1 atmosphere. The high solubility is due to the hydrogen bonding. The solubility of ammonia increase with increase of pressure and decreases with increase of temperature.

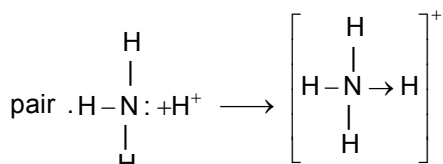


- (iv) It can be easily liquefied at room temperature by the application of pressure. The liquid ammonia is colourless and boils at -33°C . It freezes at -78°C . Liquid ammonia has a large heat of vapourisation (327 cal/g.). It is, therefore, used in ice-plants.

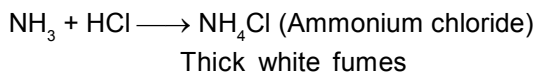
Chemical Properties : (i) Stability : It is highly stable. It decomposes into nitrogen and hydrogen at red heat or when electric sparks are passed through it .



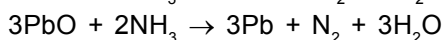
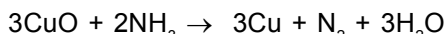
- (i) **Basic nature** : Ammonia is a Lewis base, accepting proton to form ammonium ion as it has tendency to donate an electron



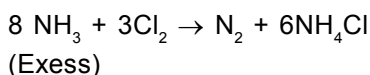
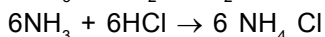
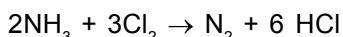
It forms salts with acids.



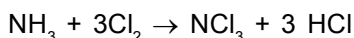
- (iii) **Oxidation** : (It is oxidised to nitrogen when passed over heated CuO or PbO.



Both chlorine and bromine oxidise ammonia.



When chlorine is in excess an explosive substance nitrogen trichloride is formed.



Hypochlorites and hypobromites oxidise ammonia to nitrogen.



The oxidation of ammonia with bleaching powder occurs on warming.



Thus, ammonia acts as a reducing agent.

Uses : (i) Liquid ammonia is used in refrigeration on account of its large heat of evaporation.

(ii) Ammonia is used in the form of ammonium hydroxide (aq. solution) in the laboratory in qualitative and quantitative analysis.

(iii) Ammonia is used for making artificial silk.

(iv) It is used as a cleansing agent for removing greese.

8.3.2 Phosphorous :

- (1) Phosphorous is largely used in match industry.
- (2) White phosphorous is used as a rat poison.

Compounds of Phosphorous :

(i) Phosphine (PH₃) :

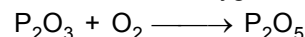
Comparison between NH₃ and PH₃ :

NH ₃	PH ₃
1. It is lighter than air	1. It is heavier than air.
2. It is not poisonous	2. It is highly poisonous
3. It forms H-bonding	3. Not form H-bonding
4. Highly soluble in water	4. Sparingly soluble in water.
5. Aqueous solution is Alkaline So Red litmus \longrightarrow Blue	5. Aq. solution is neutral.
6. Ammonia form NH ₄ OH i.e. stable	6. PH ₄ OH is unstable.
7. Form complexes	7. Does not form complexes.

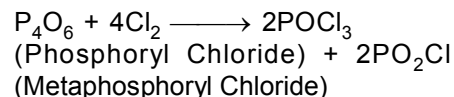
(ii) Oxides of Phosphorous :

[A] Phosphorous trioxide (P₂O₃) : (P₄O₆)

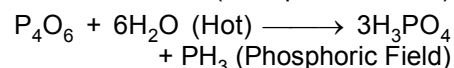
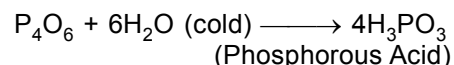
(i) Reaction with oxygen :



(ii) It burns spontaneously in chlorine :

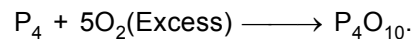


(iii) Reaction with water :

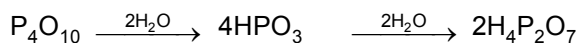


[B] Phosphorous Pentoxide (P₂O₅ or P₄O₁₀) :

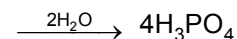
(i) Preparation : By burning phosphorous in excess of dry air. It is collected in the form of snowy powder called flower of phosphorus.



(ii) Reaction with H₂O :



Phosphorus Pentoxide Metaphosphoric Acid Phosphosphoric Acid



Ortho phosphoric Acid

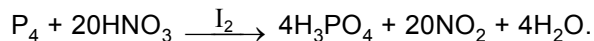
[C] Oxy Acids of Phosphorus :

(a) **Phosphorus acid (H_3PO_3) :**

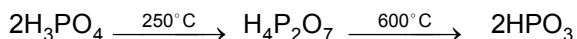
(b) **Phosphoric Acid (H_3PO_4) :**

(i) **Preparation :**

Lab Method :



(ii) **Action of heat :**



Ortho Phosphoric Acid Pyro phosphoric Acid Meta Phosphoric Acid

(c) **Pyrophosphoric Acid $H_4P_2O_7$:**

(d) **Metaphosphoric Acid (HPO_3) :**

(i) It is transparent glassy solid called glacial phosphoric Acid.

[D] Fertilisers :

(1) **Classification of Fertilizers :**

(a) **Direct Fertilizers :** These fertilizers which are directly absorbed by the plants are called direct fertilizers. These are of three types.

(i) **Nitrogenous Fertilizers :**

- (a) These are nitrogen containing fertilizer. The main function of nitrogen are :
- (b) Nitrogen causes rapid growth
- (c) Nitrogen increases protein content.
- (d) Nitrogen impart green colour to plant

(ii) **Important Nitrogenous Fertilizers :**

- (a) Urea $NH_2 - CO - NH_2$:
- (b) Calcium Cyanamide $CaCN_2$:
- (c) Ammonium sulphate $(NH_4)_2 \cdot SO_4$:

(iii) **Phosphate Fertilizers :**

- (a) These are phosphorus containing direct fertilizers.
- (b) Important function of Phosphorus :
 - (1) It stimulates root formation.
 - (2) It stimulates rapid growth.
- (c) Types of phosphate Fertilizers :
 - (1) Super phosphate of lime $[Ca(H_2PO_4)_2 + CaSO_4]$
 - (2) Triple super phosphate $3Ca(H_2PO_4)_2$.
 - (3) Thomas slag or phosphatic slag $CaSiO_3$.

(iv) **Potash Fertilizers :**

- (a) These are potassium containing direct fertilizers.
- (b) Important function of potassium :
 - (1) Helps in formation of carbohydrates
 - (2) Increases and disease resistance.
 - (3) Structural length to plants.
- (c) Types of Potash Fertilizers :
 - (1) K_2SO_4
 - (2) K_2CO_3 (wood ashes)
 - (3) KNO_3 (Indian salt petre)

(v) **Mixed Fertilizers (N.P.K.) :**

[Nitrogen + Phosphorus + Potassium.]