

P- BLOCK ELEMENTS

Topic: 1

GROUP 15 ELEMENTS (VA GROUP ELEMENTS)

LONG ANSWER QUESTIONS

1. Justify the inclusion of N and P in VA group on the basis of

- a) Electronic configuration b) Oxidation states and c) allotropy.

a) Electronic configuration

Elements belonging in Group VA (eg - N, P) all have electron configuration ending in ns^2np^3

(the superscripts total to '5' indicates there are 5 valence electrons for elements belonging to Group VA).

Nitrogen has electronic outer most orbit configuration of----- $2s^22p^3$

Nitrogen has electronic outer most orbit configuration of----- $3s^23p^3$

b) Oxidation states

These elements have five electrons in the valence shell. The loss of five electrons is quite difficult because of energy considerations. Hence they do not form ionic compounds by loss of 5 electrons. On the other hand, these elements can also gain three electrons to complete their octets. But gain of 3 electrons is also not energetically favorable. However, they do form N^{3-} and P^{3-} ions by gaining three electrons from highly electropositive elements, e.g. Mg_3N_2 , Ca_3P_2 .

In addition to - 3 oxidation state, the elements of group 15 exhibit +3 and +5 oxidation states. For e.g., phosphorus forms pentahalides such as PF_5 , PCl_5 (+5 oxidation state) and trihalides PCl_3 , PF_3 (+3 oxidation state).

Nitrogen exhibits various oxidation states from -3 to +5 in its hydrides, oxides and oxo acids.

For e.g.,

Compound	Oxidation state
NH ₃ Ammonia	- 3
N ₂ H ₄ Hydrozine	- 2
N ₂ Nitrogen	0

Compound	Oxidation state
N ₂ O Nitrous Oxide	+ 1
NO Nitric Oxide	+ 2
N ₂ O ₃ Nitrogen trioxide	+ 3
N ₂ O ₄ Nitrogen tetraoxide	+ 4
N ₂ O ₅	+ 5

c) Allotropy:

Nitrogen shows two allotropic forms, Alfa form and Beta form.

Phosphorous shows allotropy

For e.g.,

Phosphorus exists as - white, black or red phosphorus allotropic forms.

All elements of group VA elements except Bismuth show allotropy.

2. Distinguish the gradation in the following properties of VA group elements –

- a) Physical states b) Catenation c) Metallic nature**

a) Physical states:

Nitrogen is a gas, Phosphorous is a waxy solid andn As, Sb and Bi are solids.

b)Catenation

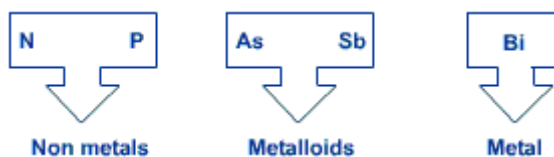
The elements of group 15 also show a tendency to form bonds with itself known as catenation. All these elements show this property but to a much smaller extent than carbon. For e.g., hydrazine (H₂N-NH₂) has two N atoms bonded together, hydrazoic acid,

(N₃H), has three N-atoms, azide ion, N_3^- , has also three N atoms bonded together, while diphosphine (P₂H₄) has two phosphorus atoms bonded together. The lesser tendency of elements of group 15 to show catenation in comparison to carbon is their low (M-M) bond dissociation energies.

Bond	C - C	N - N	P - P	As - As
Bond energy	353.3	163.8	201.6	147.4

c) Metallic character

The elements of group 15 are less metallic. However on going down the group, the metallic character increases from N to Bi. For e.g., N and P are non-metallic, As and Sb are partly non-metallic while Bi is a metal.



3. Give a detailed account of the general characteristics of Nitrogen family elements. Hence justify their inclusion in the same family.

Ans: The nitrogen family is element group 15 of the periodic table. The nitrogen family consists of nitrogen, phosphorus, arsenic, antimony and bismuth... Nitrogen family elements consist of atoms having 5 electrons in their outer energy level. As you move down the nitrogen family: atomic radius increases, ionic radius increases, ionization energy decreases, and electronegativity decreases. Nitrogen family elements often form covalent compounds, usually with the oxidation numbers +3 or +5. Nitrogen and phosphorus are nonmetals. Arsenic and antimony are metalloids. Bismuth is a metal. Except for nitrogen, the elements are solid at room temperature. Except for nitrogen and bismuth, the elements exist in two or more allotropic forms. Element facts include crystal data for the most common allotropes and data for white phosphorus.

Some important physical constants of group 15 elements

	N	P	As	Pb	Bi
Atomic radius (pm)	70	110	120	140	150
Ionic radius (pm)	171 (N ³⁻)	212 (P ³⁻)	222 (As ³⁻)	76 (Sb ³⁺)	
Ionisation energy IE ₁ (kJ mol ⁻¹)	1402	1012	947	834	703
IE ₂	2856	1903	1798	1594	1610
IE ₃	4577	2910	2736	2443	2446
Electronegativity	3.0	2.1	2.0	1.9	1.9
Melting point (K)	63	317.1	1089	904	544.4
Boiling point (K)	77	553.5	888	1860	1837
Density (g cm ⁻³)	0.879	0.879	5.778	6.697	9.808

The important physical characteristics are discussed below:

Atomic and ionic radii

The atomic and ionic radii of group 15 elements are smaller than the atomic radii of the corresponding group 14 elements. This is because of increased nuclear charge. On going down the group, the atomic radii increase due to the increase in number of shells.

Melting and boiling points

Melting points (except for antimony and bismuth) and boiling points increase on going down the group from N to Bi.

Ionization energies

The first ionization energies of the group 15 elements are higher than the corresponding members of the group 14 elements.

Explanation:

The larger ionization energy is due to greater nuclear charge, small size and stable configuration of the atoms of group 15 elements. The electronic configuration of atoms of group 15 is half filled energies. On going down the group, the ionization energies decrease. This is due to increase in atomic size and screening effect, which outweigh the effect of increased nuclear charge.

np_x^1, np_y^1, np_z^1 and are stable. Therefore, they have high ionisation

Electronegativity

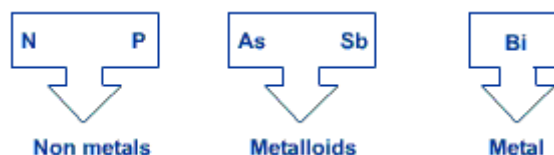
The electronegativity values of elements (of group 15) are higher than the corresponding elements of group 14.

Explanation:

The elements of group 15 have smaller size and greater nuclear charge of atoms and therefore they have higher electronegativity values. On going down the group the electronegativity value decreases. This is due to increase in size of the atoms and shielding effect of inner electron shells on going down the group.

Metallic character

The elements of group 15 are less metallic. However on going down the group, the metallic character increases from N to Bi. For e.g., N and P are non-metallic, As and Sb are partly non-metallic while Bi is a metal.



Catenation

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Bond	C - C	N - N	P - P	As - As
Bond energy	353.3	163.8	201.6	147.4

Allotropy

Except nitrogen and bismuth, all other elements of this group show allotropy.

For e.g.,

- Phosphorus exists as - white, black or red phosphorus
- Arsenic exists as - yellow or grey arsenic
- Antimony exists as - yellow or silvery grey
- allotropic forms.

Oxidation states

These elements have five electrons in the valence shell. The loss of five electrons is quite difficult because of energy considerations. Hence they do not form ionic compounds by loss of 5 electrons. On the other hand, these elements can also gain three electrons to complete their octets. But gain of 3 electrons is also not energetically favorable. However, they do form N^{3-} and P^{3-} ions by gaining three electrons from highly electropositive elements, e.g. Mg_3N_2 , Ca_3P_2 .

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For e.g.,

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NO Nitric Oxide	+ 2
N ₂ O ₃ Nitrogen trioxide	+ 3
N ₂ O ₄ Nitrogen tetraoxide	+ 4
N ₂ O ₅	+ 5

4. Explain the structure of Ammonia and Phosphine.

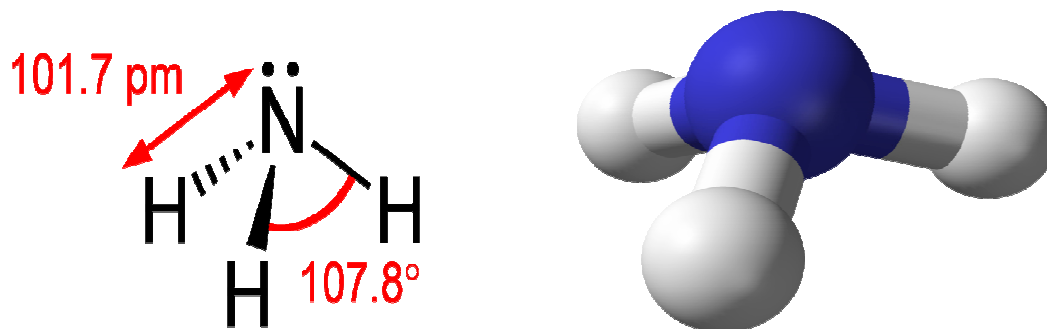
Ans: Structure of Ammonia:

The ammonia molecule has a trigonal pyramidal shape with a bond angle of 107.8°, as predicted by the valence shell electron pair repulsion theory (VSEPR theory).

The central nitrogen atom has five outer electrons with an additional electron from each hydrogen atom. This gives a total of eight electrons, or four electron pairs which are arranged tetrahedrally. Three of these electron pairs are used as bond pairs, which leaves one lone pair of electrons.

The lone pair of electrons repel more strongly than bond pairs, therefore the bond angle is not 109.5° as expected for a regular tetrahedral arrangement, but is measured at 107.8°.

The nitrogen atom in the molecule has a lone electron pair, which makes ammonia a base, a proton acceptor. This shape gives the molecule a dipole moment and makes it polar. The molecule's polarity and, especially, its ability to form hydrogen bonds, makes ammonia highly miscible with water.



Structure of Phophene:

PH_3 is a trigonal pyramidal molecule with C_{3v} molecular symmetry. The length of the P-H bond 1.42 Å, the H-P-H bond angles are 93.5° .

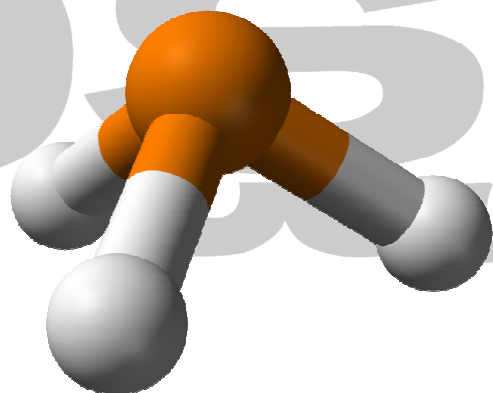
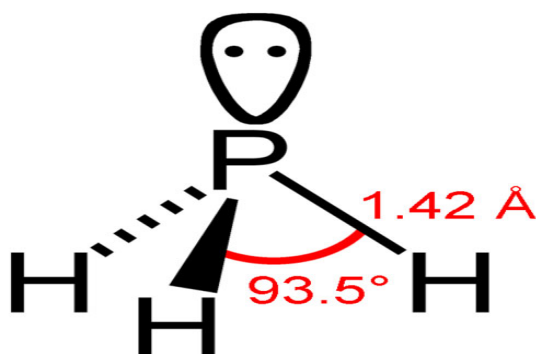
The dipole moment is 0.58 D, which increases with substitution of methyl groups in the series: CH_3PH_2 , 1.10 D; $(\text{CH}_3)_2\text{PH}$, 1.23 D; $(\text{CH}_3)_3\text{P}$, 1.19 D.

In contrast, the dipole moments of amines decrease with substitution, starting with ammonia, which has a dipole moment of 1.47 D.

The low dipole moment and almost orthogonal bond angles lead to the conclusion that in PH_3 the P-H bonds are almost entirely $p\sigma(\text{P}) - s\sigma(\text{H})$ and the lone pair contributes only a little to the molecular orbitals.

The high positive chemical shift of the phosphorus atom in the ^{31}P NMR spectrum accords with the conclusion that the lone pair electrons occupy the 3s orbital and so are close to the P atom (Fluck, 1973).

This electronic structure leads to a lack of nucleophilicity and an inability to form hydrogen bonds.



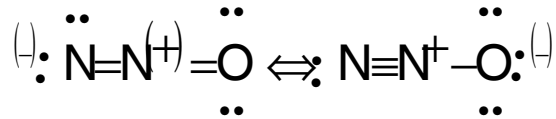
5. Discuss the structures of oxides of nitrogen.

Oxides of Nitrogen:

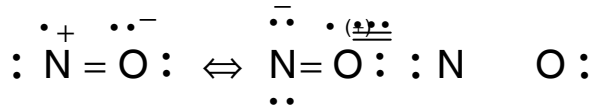
Oxides of N_2 are endothermic (except N_2O_5) and acts as better oxidants. Except N_2O_5 all are gases.

a) N_2O (Laughing gas):

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

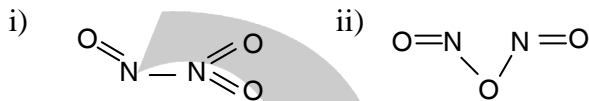


b) Structure of NO : NO has 11 valence electrons (N → 5, O → 6). Presence of odd, electron makes it as paramagnetic. It doesn't dimerise due to delocalised odd electron.



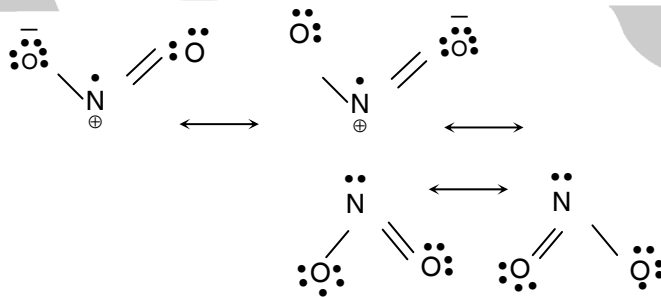
c) Nitrogen sesquioxide or dinitrogen trioxide (N₂O₃) :

Structure:

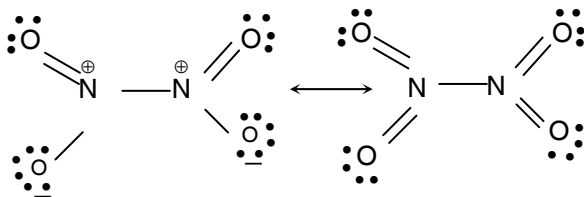


d) Nitrogen Dioxide:

Structure: NO₂ has angular structure with a bond angle of 132°. It possesses a three electron bond and hence it is coloured and paramagnetic.



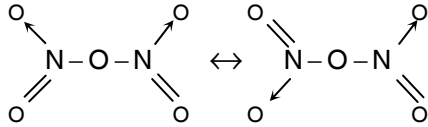
e) The structure of N₂O₄ :



f) **Nitrogen pentoxide:**

Structure:

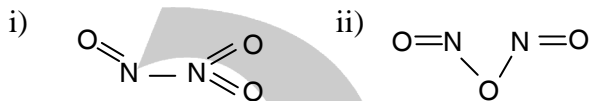
It is an ionic solid i.e, Nitronium nitrate (NO_2^+ , NO_3^-)



6. **In what way trioxides and pentoxides of Nitrogen and phosphorus differ?**

1) **Nitrogen sesquioxide or dinitrogen trioxide (N_2O_3) :**

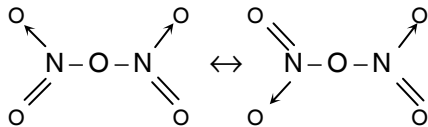
Structure:



2) **Nitrogen pentoxide:**

Structure:

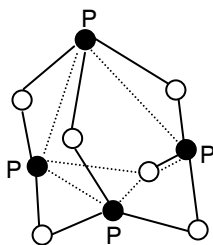
It is an ionic solid i.e, Nitronium nitrate (NO_2^+ , NO_3^-)



3) **Structure of phosphorous trioxide (P_4O_6):**

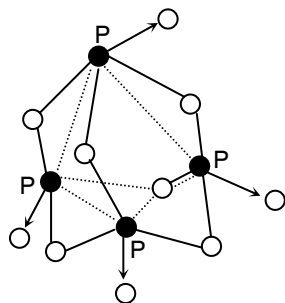
- P_2O_3 and P_2O_5 exist as dimers.

P_4O_6



Phosphorus is linked to 3 oxygen

4) **Structure of phosphorous Pentoxide (P₄O₆ and P₄O₁₀):**



Phosphorus is linked to 4 oxygen

- It is interesting to note that the oxides of nitrogen and phosphorous are chemically similar but structurally different.
- The trioxide and pentoxides of phosphorous are dimers whereas nitrogen oxides are monomers.

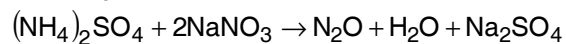
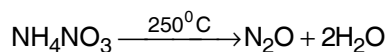
7. Write the preparation and properties and structures of any three of the oxides of Nitrogen.

Oxides of Nitrogen:

Oxides of N₂ are endothermic (except N₂O₅) and act as better oxidants. Except N₂O₅ all are gases.

a) N₂O (Laughing gas): First prepared by Priestley.

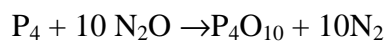
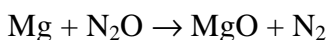
Berthelot prepared it from Ammonium nitrate or ammonium sulphate and sodium nitrate.



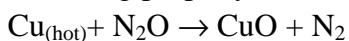
It is colourless neutral gas.

Fairly soluble in cold water.

It is incombustible but supports combustion of Mg and P.

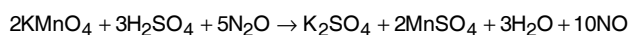


Oxidising property: - It oxidises metals.

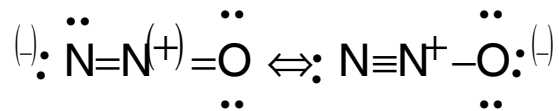


Mixture of O₂ and N₂O is used as anaesthetic in surgery and dentistry.

In the presence of acidified potassium permanganate it undergoes oxidation to give nitric oxide.



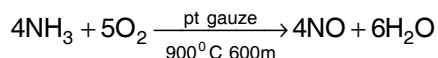
Structure: N₂O is hybrid of following structures. It is a linear molecule.



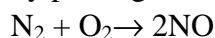
b) Nitric oxide (NO) Nitrogen monoxide : (Priestley)



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



3) By passing electric arc through N₂ and O₂

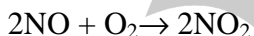


Properties:

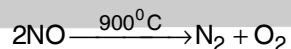
NO is colourless gas and heavier than air.

At 12 K it freezes to Blue solid & its M.P is 1232 K.

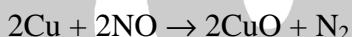
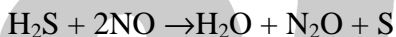
On reaction with oxygen it gives reddish brown fumes.



NO is most thermally stable oxide of N₂.



Oxidising properties:



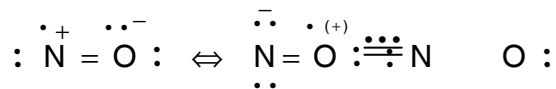
In the manufacture of H₂SO₄ by lead chamber process NO is used as catalyst.

Structure: NO has 11 valence electrons

(N → 5, O → 6).

Presence of odd, electron makes it as paramagnetic.

It doesn't dimerises due to delocalised odd electron.



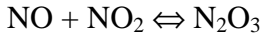
In liquid and solid states it dimerises hence it is diamagnetic.

c) Nitrogen sesquioxide or dinitrogen trioxide (N₂O₃) :

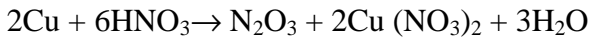
N₂O₃ is a hydride of nitrous acid.



By cooling a mixture of NO and NO₂ in equimolar ratio to – 20°C N₂O₃ is obtained.



On action of Cu on HNO_3 N_2O_3 is obtained.

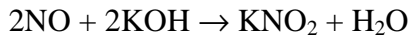


It is blue liquid and a pale blue solid.

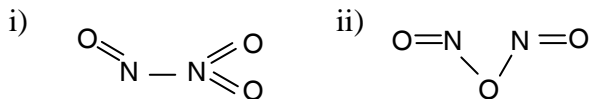
M.P is -102°C .

It is acidic oxide.

It's salts are called as nitrites.



Structure:

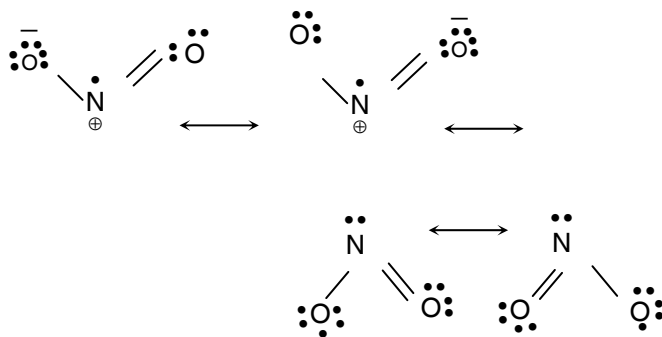


d) Nitrogen Dioxide:

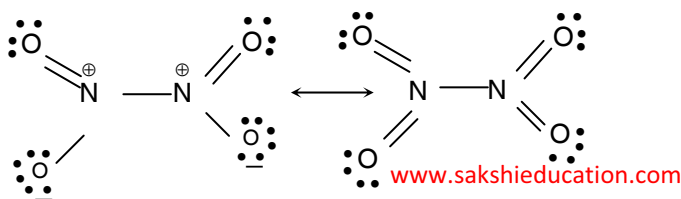
- It is reddish brown gas.
- It dimerises to dinitrogen tetraoxide which is colourless solid.
- $$2\text{NO}_2 \xrightarrow{-11^\circ\text{C}} \text{N}_2\text{O}_4$$

Brown Paramagnetic Colourless solid diamagnetic
- Reduction of conc nitric acid with metals like Cu, Ag gives NO_2 .
- $\text{Cu} + 4\text{HNO}_3 \rightarrow 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$
- Lead nitrate on heating gives NO_2
- $\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$
- NO_2 dissolves in water to give nitrous and nitric acids hence it is called as mixed anhydride of HNO_2 and HNO_3 .
- $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$

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.

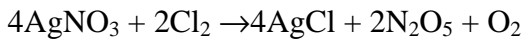
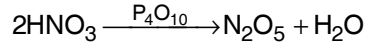


The structure of N_2O_4 :



e) Nitrogen pentaoxide:

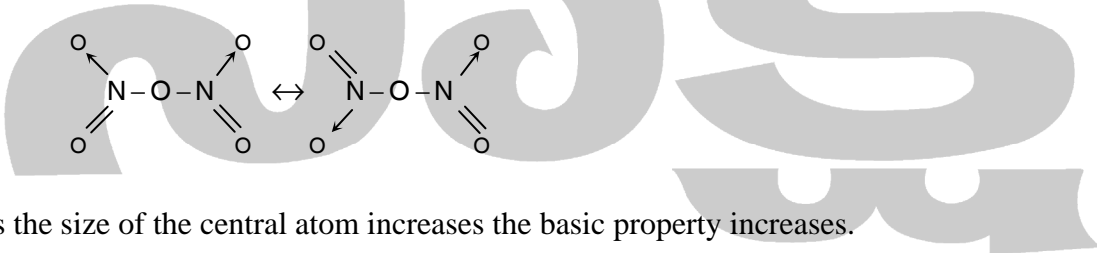
On dehydration of Nitric acid with the help of phosphorous pentoxide N_2O_5 is obtained.



- N_2O_5 is white solid.
- M.P. $35^\circ C$.
- 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^-)

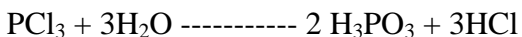
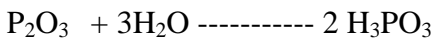


As the size of the central atom increases the basic property increases.

8. Explain the preparation and structures of phosphorous acids.

a) Orthophosphorus acid: H_3PO_3

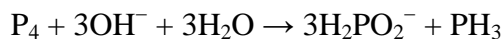
It is a dibasic acid. Preparation of H_3PO_3 by the addition of cold water on phosphorus trioxide or phosphorus trichloride.



It is a white crystalline solid with garlic state

b) Hypophosphorus acid: H_3PO_2

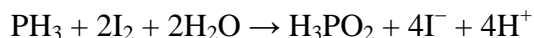
The acid is prepared industrially via a two step process. Hypophosphite salts of the alkali and alkaline earth metals result from treatment of white phosphorus with hot aqueous solution of the appropriate hydroxide, e.g. $\text{Ca}(\text{OH})_2$.



The free acid may be prepared by the action of a strong acid on these hypophosphite salts.



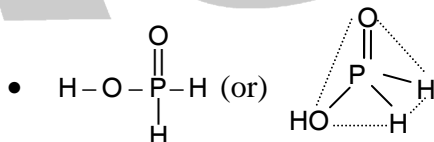
Alternatively, H_3PO_2 arises by the oxidation of phosphine with iodine in water.



HPA is usually supplied as a 50% aqueous solution

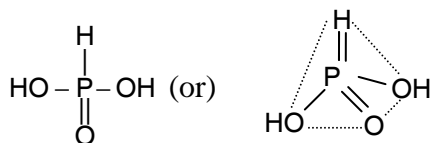
1. Hypophosphorous acid: (H_3PO_2):

- 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 :**



2. 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 :**

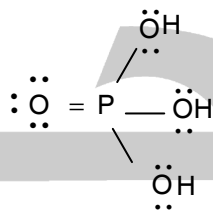


3. Orthophosphoric acid (H₃PO₄):

- Ca₃(PO₄) with H₂SO₄ gives H₃PO₄.
- P₂O₅ on hydrolysis gives H₃PO₄.
- Forms three types of salts (basicity is three).
- Dihydrogen phosphate (H₂PO₄⁻).
- Hydrogen phosphate (HPO₄²⁻).
- Phosphate (PO₄³⁻).
- It is syrupy liquid due to hydrogen bonding.
- The acid loses water steadily on heating.



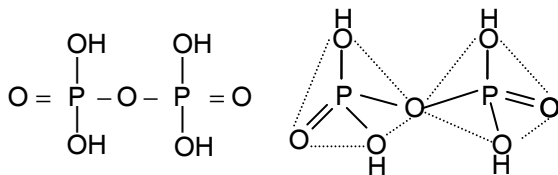
- Structure :



Used in the preparation of HBr and HI.

4. Pyrophosphoric acid: (H₄P₂O₇):

- It forms salts of type M₄P₂O₇ and M₂H₂P₂O₇.
- Ca₂P₂O₇ is used in fluoride tooth pastes.
- Na₂H₂P₂O₇ is used in making bread.
- It is a Tetrabasic acid.
- Structure :

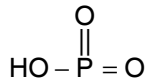


5. Metaphosphoric acid (HPO₃):

- By heating H₃PO₄ or H₄P₂O₇ 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 (PO₃⁻) ions doesn't exist where as it forms a ring

compounds like triphosphates, tetraphosphates or polyphosphates.

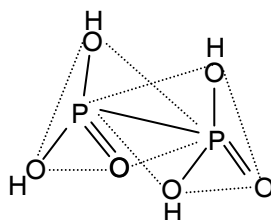
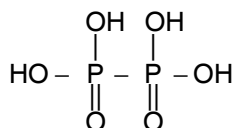
- It's polymeric sodium metaphosphates are called as Graham's salt, Kurrol's salt and mandrel's salt (NaPO_3)_n.
- It is a monobasic acid.
- Structure :



6. Hypophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$):

It is a tetrabasic acid.

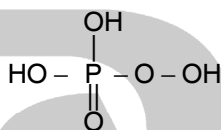
Structure:



7. Peroxy phosphoric acid (H_3PO_5):

It is a Tribasic acid.

Structure:

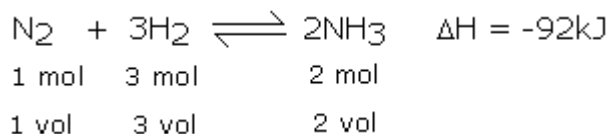


9. Explain the Haber's process of preparation of ammonia.

Ans: **Manufacture of Ammonia:**

Haber's process

The manufacture of ammonia by Haber's process involves the direct combination of nitrogen and hydrogen.



This reaction is, (a) reversible, (b) exothermic, and (c) proceeds with a decrease in volume. According to the Le Chatelier's principle, the favorable conditions for the formation of ammonia are,

Low temperature

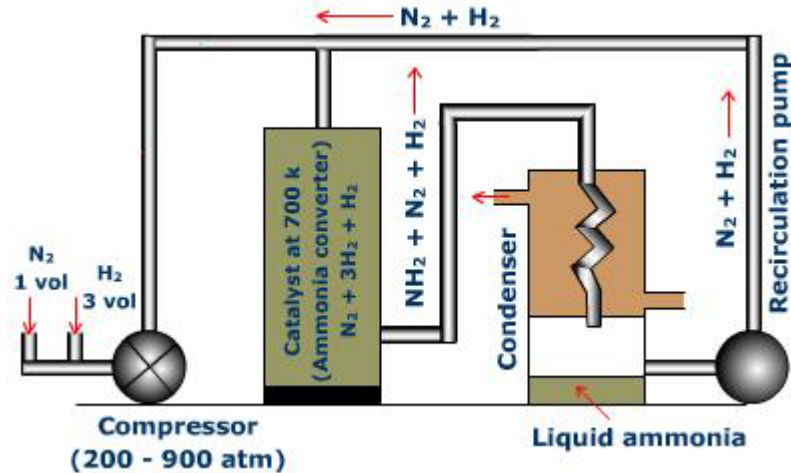
The temperature should be remain as low as possible, (although at unusually low temperatures, the rate of reaction becomes slow). It has been found that the temperature, which optimizes the yield of ammonia for the reaction, is maximum at about 500°C.

High pressure

Since Haber's process proceeds with a decrease in volume, it is favored by high pressure. In actual practice, a pressure of 200 - 900 atmospheres is employed.

Catalyst

A catalyst is usually employed to increase the speed of the reaction. Finely divided iron containing molybdenum or alumina is used as a catalyst. Molybdenum or alumina (Al_2O_3) acts as a promoter and increases the efficiency of the catalyst. A mixture of iron oxide and potassium aluminate has been found to work more effectively.

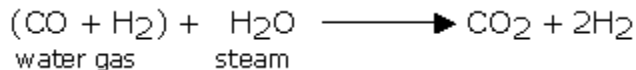
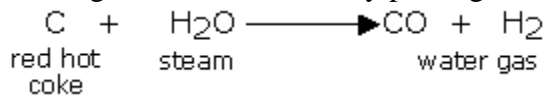


Manufacturing plant employed in Haber's process

Source of raw materials

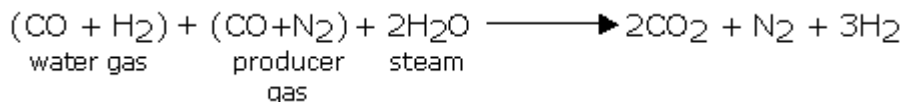
The nitrogen and hydrogen gases used as the raw material in Haber's process are obtained as follows.

- Nitrogen is obtained from the liquid air and hydrogen from water by electrolysis.
- Hydrogen may be obtained from water gas (mixture of CO and H_2) by Bosch process.
- Water gas can be obtained by passing steam over red hot coke.



By bubbling the mixture through water, CO_2 is removed.

- A mixture of nitrogen and hydrogen may be obtained by treating a mixture of producer gas ($\text{CO} + \text{N}_2$), water gas ($\text{CO} + \text{H}_2$) with steam in the presence of ferric oxide - chromium oxide catalyst at 450°C .



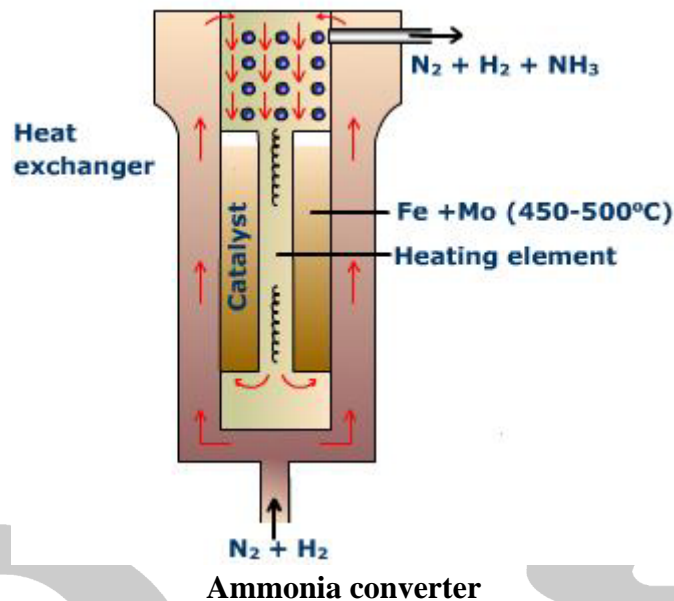
Carbon dioxide is removed by bubbling through water under pressure.

Plant

The plant, which manufactures ammonia, has the following components and processes.

Compressor

A mixture of nitrogen and hydrogen is compressed to 200-900 atmosphere pressure, in the ratio 1:3 (by volume). The compressed gas is sent to ammonia converter.



Converter

Ammonia converter is made from chrome-vanadium steel. It is usually 1.3 meter high and 1 meter in diameter. The converter is provided with a heat exchanger in the upper portion and the catalyst is packed in the central portion of the converter. There is an arrangement for heating the gas mixture. After the gas mixture enters through the inlet at the bottom, the gases circulate around the catalyst maintained at $450-500^\circ C$ and then pass through to the heat exchanger. The gases finally enter the catalyst chamber to give ammonia. Before entering the condensers the product as well as the unreacted gases pass through the pipes of the heat exchanger and transfer their heat to the incoming gas mixture containing nitrogen and hydrogen.

Condensers

This cools and liquefies ammonia. The condensed ammonia, called 'liquor ammonia' is filled into cylinders under pressure.

Re-circulating pump

Some of the nitrogen and hydrogen gases escape condensation and are re-circulated through the converter.

10. Explain the Ostwald's Process of manufacture of Nitric Acid.

Ans: INTRODUCTION

Nitric acid is a strong mineral acid. It is a mono-basic acid. It is a strong oxidizing agent and can oxidize metals and nonmetals easily. It is used in the manufacture of fertilizers, silk industry, explosive materials such as (T.N.T) etc.

INDUSTRIAL PREPARATION OF NITRIC ACID

On industrial scale, nitric acid can be prepared by the following methods.

- (a) **CHILLI-SALT PETER'S METHOD:** By NaNO_3
- (b) **BRIKLAND-EYDE'S METHOD:** By using air
- (c) **OSTWALD'S METHOD :** By ammonia

OSTWALD'S METHOD

Materials used:

- Ammonia gas
- Water
- Oxygen gas

CATALYST

Platinum

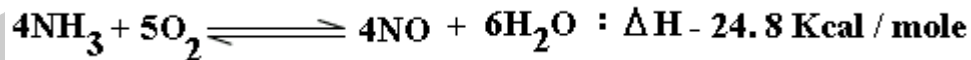
DETAILS OF PROCESS

First step

PRIMARY OXIDATION (formation of nitric acid)

Oxidation of ammonia is carried out in a catalyst chamber in which one part of ammonia and eight parts of oxygen by volume are introduced. The temperature of chamber is about 600°C . This chamber contains platinum gauze which serves as catalyst.

CHEMISTRY OF PRIMARY OXIDATION



Oxidation of ammonia is reversible and exothermic process. Therefore according to Le- chatelier's principle, a decrease in temperature favour reaction in forward direction. In primary oxidization 95% of ammonia is converted into nitric oxide (NO). **Second step**

SECONDARY OXIDATION (formation of nitrogen dioxide)

Nitric oxide gas obtain by the oxidation of ammonia is very hot. In order to reduce its temperature , it is passed through a heat exchanger where the temperature of nitric oxide is reduce to 150°C . Nitric oxide after cooling is transferred to another oxidizing tower where at about 50°C it is oxidizing to NO_2 .



Third step

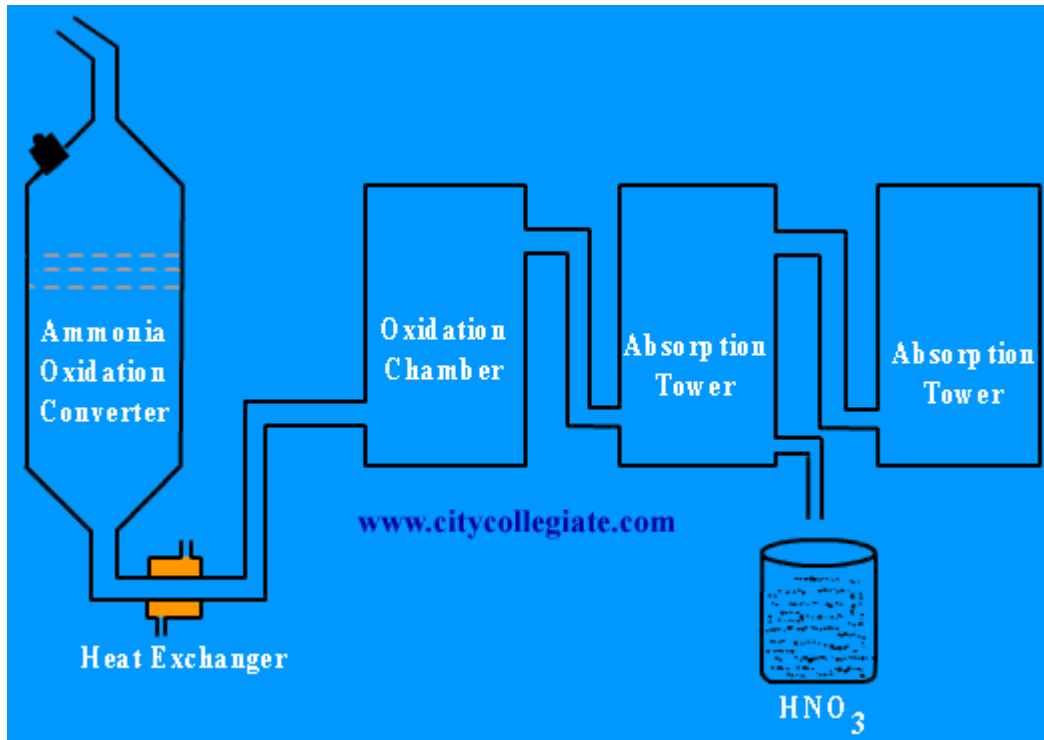
ABSORPTION OF NO_2 (formation of HNO_3)

Nitrogen dioxide from secondary oxidation chamber is introduced into a special absorption tower.

NO_2 gas passed through the tower and water is showered over it. By the absorption, nitric acid is obtained.



Nitric acid so obtain is very dilute. It is recycled in absorption tower so that more and more NO_2 get absorbed. HNO_3 after recycle becomes about 68% concentrated.



Fourth step

CONCENTRATION

In order to increase the concentration of HNO_3 , vapour of HNO_3 are passed over concentrated H_2SO_4 . Being a dehydrating agent H_2SO_4 absorbs water from HNO_3 and concentrated HNO_3 is obtained.

11. Explain the preparation of superphosphate of lime. Why is it converted to 'triple phosphate' of lime?

Ans: Superphosphate of lime is also known as calcium superphosphate. This is one of the few water soluble phosphates. A mixture of calcium dihydrogen phosphate [$\text{Ca}(\text{H}_2\text{P}_0_4)_2$] and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is known as superphosphate of lime.

Superphosphate is made by treating well powdered phosphate rock (calcium phosphate) with calculated quantities of commercial concentrated sulphuric acid (chamber acids)"



(The composition of the super phosphate may change and need not be always represented by this formula only).

Industrial method: The plant used for the preparation of superphosphate of lime is shown in fig 1.5.

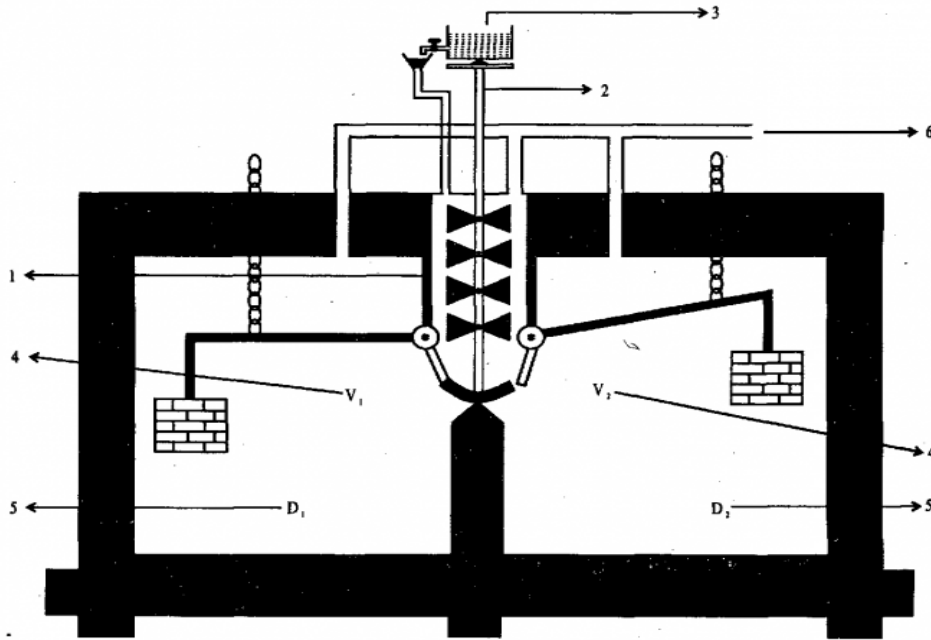


Fig : 1.5. Manufacture of superphosphate of lime.

1. Mixer 2. Stirrer 3. Chamber acid 4. Valves 5. Brick work Dens 6. Waste gases.

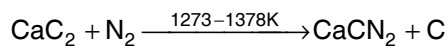
The phosphate rock is ground to a fine powder. It is charged into a cast iron mixer. A calculated quantity of conc. H₂SO₄ (Chamber acid) is added. The reaction mixture is stirred with blades present in the mixer. When the reaction had started it is dumped into one of the two dens, D₁ and D₂, through either the valve V₁ or the valve V₂. The reaction is allowed to take place for 24-36 hours in the dens. In this period temperature rises to about 373 -383 K. [The carbonate and the fluoride impurities in the phosphate rock react with H₂SO₄ and liberate CO₂ and HF gases. They escape through the outlet at the top]. The final product is a hard mass (due to the presence of gypsum). This mass is crushed to fine powder and sold as superphosphate of lime.

Uses: - Superphosphate of lime is a good phosphatic fertilizer. The CaSO₄ is an insoluble waste product and is of no value to the plants. To avoid this waste product CaSO₄, superphosphate is changed into "**triple phosphate**" which completely dissolves in water.

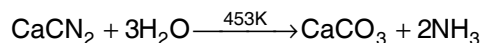
12. Explain cyanamide process and mention important uses of ammonia.

Cyanamide process:

- Calcium carbide on reaction with nitrogen gas at 1273K in the presence of CaCl₂ or CaF₂ as catalyst gives calcium cyanamide and graphite mixture. This is called as nitrolim.

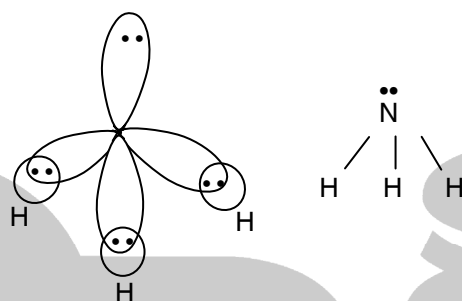


- Hydrolysis of cyanamide with steam gives NH₃.



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 Ostwald's process), explosive like ammonium nitrate, ammonia is required.
- Liquor ammonia is useful as a good solvent for both ionic as well as covalent compounds.
- Structure: Pyramidal in shape, Hybridisation sp^3 .



SHORT ANSWER QUESTIONS

1. Write the names and electronic configuration of VA elements.

Properties of the Group VA Elements.

Element	Symbol	Electron Configuration
Nitrogen	N	$[\text{He}]2s^22p^3$
Phosphorus	P	$[\text{Ne}]3s^23p^3$
Arsenic	As	$[\text{Ar}]4s^23d^{10}4p^3$
Antimony	Sb	$[\text{Kr}]5s^24d^{10}5p^3$
Bismuth	Bi	$[\text{Xe}]6s^24f^{14}5d^{10}6p^3$

2. What is allotropy? Explain it VA group.

Ans: Allotropy: Allotropy or allotropism is the property of some chemical elements to exist in two or more different forms, known as allotropes of these elements. Allotropes are different structural modifications of an element; the atoms of the element are bonded together in a different manner.

Except nitrogen and bismuth, all other elements of this group show allotropy.

For e.g.,

- Phosphorus exists as - white, black or red phosphorus
- Arsenic exists as - yellow or grey arsenic
- Antimony exists as - yellow or silvery grey
- allotropic forms.

3. What is catenation how does it vary in group 15?

Ans: Catenation

The elements of group 15 also show a tendency to form bonds with itself known as catenation. All these elements show this property but to a much smaller extent than carbon. For e.g., hydrazine ($\text{H}_2\text{N-NH}_2$) has two N atoms bonded together, hydrazoic acid, (N_3H), has three N-atoms, azide ion, N_3^- , has also three N atoms bonded together, while diphosphine (P_2H_4) has two phosphorus atoms bonded together. The lesser tendency of elements of group 15 to show catenation in comparison to carbon is their low (M-M) bond dissociation energies.

Bond	C - C	N - N	P - P	As - As
Bond energy	353.3	163.8	201.6	147.4

4. What are the oxidation states exhibited by N_2 ? Give one example each.

Nitrogen shows various oxidation states because of small size and high electronegativity. It shows

- 3 in NH_3 .
- 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

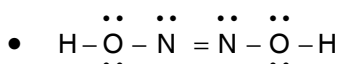
5. Mention important oxoacids of N. Write their structures.

Oxyacids of Nitrogen:

Hypo nitrous acid ($\text{H}_2\text{N}_2\text{O}_2$):

- It is hydrate of N_2O
- Its salts are called hyponitrites.
- Acid and its salts are reducing agent.

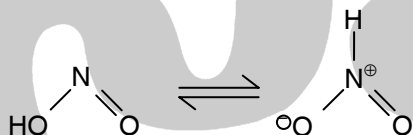
Structure:



Nitrous acid (HNO_2):

- Dilute acids on reaction with Alkali nitrites gives HNO_2 .
- It is highly unstable.
- Salts are called as nitrites and are stable.
- Itself and its salts are oxidizing and reducing agents.
- Eg: It oxidizes $\text{FeSO}_4 \rightarrow \text{Fe}(\text{SO}_4)_3$
- It reduces $\text{I}_2 \rightarrow \text{I}^-$ and $\text{KMnO}_4 \rightarrow \text{Mn}^{2+}$

Structure:



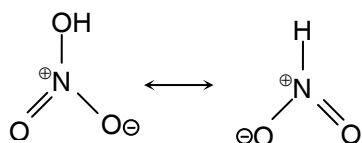
Mono basic

Used in the preparation of Ozodyes.

Nitric acid (HNO_3) (Aqua fortis):

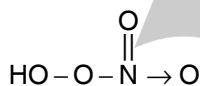
- 1 : 1 ratio of KNO_3 , H_2SO_4 gives HNO_3 .
- Manufactured by Ostwald and Birkland – Eyde process.
- In ostwald process the raw material is Ammonia.
- Catalyst in ostwald process is platinum guaze.
- Ammonia is oxidized in the process.
- 96 – 98 % HNO_3 is called as fuming nitric acid.
- With Cu dil HNO_3 gives NO with conc. HNO_3 gives NO_2 .
- Due to dissolved oxides of Nitrogen it is yellow.
- 1 : 3 mixture of conc. HNO_3 and HCl is called as aqua regia, which dissolves noble metals like Au, Pt, Rh etc.,.
- NOCl produced is responsible for the solubility of Au.
- $\text{HNO}_3 + 3\text{HCl} \rightarrow \text{Cl}_2 + 2\text{H}_2\text{O} + 2\text{NOCl}$

- Mixture of HNO_3 and H_2SO_4 is called as nitration mixture.
- HNO_3 is good oxidizing agent.
- $\text{S} \rightarrow \text{H}_2\text{SO}_4$; $\text{P} \rightarrow \text{H}_3\text{PO}_4$; $\text{C} \rightarrow \text{CO}_2$
- Due to formation of xanthoproteins it produces yellow stains on skin.
- Metals like Al become passive (in active) with conc. HNO_3 due to formation of their oxide layer.
- It is used to prepare fertilizers like Ammonium nitrate (NH_4NO_3) and explosives like TNT (trinitrotoluene) teargas CCl_3NO_3 .



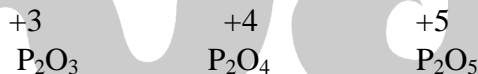
Pernitric acid:

- HNO_4 is called as per nitric acid.



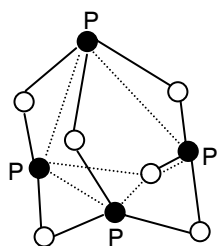
6. Draw the structures of P_4O_6 and P_4O_{10} .

Ans: Phosphorous forms the following oxides.



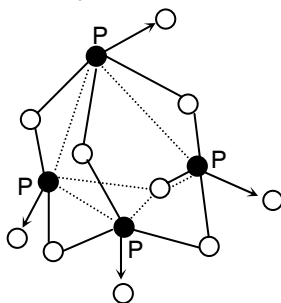
P_2O_3 and P_2O_5 exist as dimmers P_4O_6 and P_4O_{10} .

P_4O_6



Phosphorus is linked to 3 oxygens

P_4O_{10}

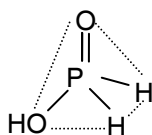


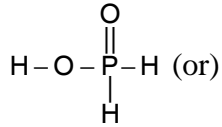
Phosphorus is linked to 4 oxygens

7. Explain the acids of phosphorous.

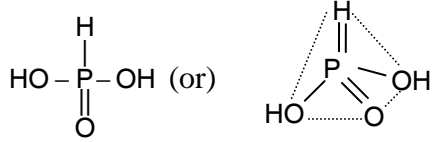
Ans: Oxyacids of phosphorous:

1. Hypo phosphorous acid : (H_3PO_2)

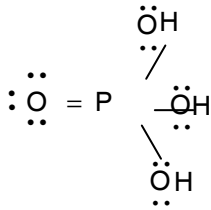




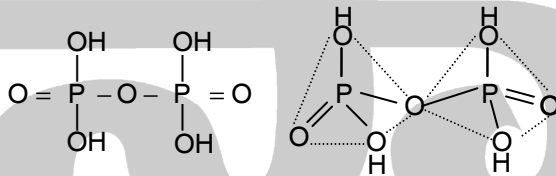
2. Ortho Phosphorous acid: (H₃PO₃)



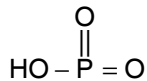
3. Orthophosphoric acid (H₃PO₄):



Pyrophosphoric acid: (H₄P₂O₇):



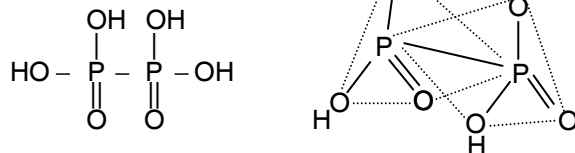
Metaphosphoric acid (HPO₃):



• **Hypophosphoric acid (H₄P₂O₆):**

It is a tetrabasic acid.

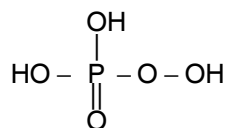
Structure:



Peroxy phosphoric acid (H₃PO₅):

It is a Tribasic acid.

Structure:



VERY SHORT ANSWER QUESTIONS

1. Give the electronic configuration of P and As.

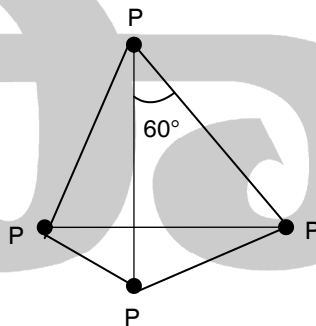
Ans:

Element	Symbol	Electron Configuration
Phosphorus	P	$[\text{Ne}]3s^23p^3$
Arsenic	As	$[\text{Ar}]4s^23d^{10}4p^3$

2. Write the structure of P₄.

Ans:

P₄ has a regular tetrahedral structure having one P atom at each vertex of the tetrahedron. The bond angle $\angle\text{PPP}$ 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 its electronegative value is high.



3. How does the stability of hydrides of VA group elements decrease?

Ans:

These elements form hydrides of the type MH₃

NH₃(Ammonia) PH₃(Phosphine)

AsH₃(Arsine) SbH₃(Stibine)

BiH₃ (Bismuthine)

NH₃ to BiH₃ the stability decreases

4. Why do nitrogen not form pentahalides?

Ans: 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.

5. What is the function of CaCl₂ in cyanamide process?

Ans: It acts a catalyst.