By- SHAILENDRA SHUKLA SIR

The p-Block Elements

Inert Pair Effect

The general outer shell electronic configuration of p-block elements is ns^2, np^{1-6}. Here, due to insufficient screening effect of the intervening electrons of d and f-orbitals, the nuclear attraction on paired electrons of the s-orbital of outermost shell gets highly increased. Hence, they require very large amount of energy for their unpairing, which is not available under reaction conditions and therefore, this electron pair shows reluctance from bond formation and behave like inert pair. This effect is called Inert Pair Effect.

Consequence of Inert Pair Effect

Due to Inert Pair Effect, heavier p-block elements also exhibit a lower oxidation state of (G-2), along with their normal group oxidation state (G). Here, the stability of lower oxidation state goes on increasing on moving down the group. For example,

Heavier elements of group 13, show a lower oxidation state of +1, along with the normal group oxidation state +3 and stability of +1 oxidation state goes on increasing on moving down the group. Here, For Al, Ga and In, +3 oxidation state is more stable than +1 oxidation state, while for Tl, +1 oxidation state is more stable than +3 oxidation state.

Al, Ga, In } +3 state is more stable than +1 state

Tl } +1 state is more stable than +3 state

Similarily, heavier elements of group 14, show a lower oxidation state of +2, along with the normal group oxidation state +4 and stability of +2 oxidation state goes on increasing on moving down the group. Here, for Si, Ge and Sn, +4 oxidation state is more stable than +2 oxidation state, while for Pb, +2 oxidation state is more stable than +4 oxidation state.

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Si, Ge, Sn } +4 state is more stable than +2 state

Pb } +2 state is more stable than +4 state

In the same way, heavier elements of group 15, show a lower oxidation state of +3, along with the normal group oxidation state +5 and stability of +3 oxidation state goes on increasing on moving down the group. Here, for P, As and Sb, +5 oxidation state is more stable than +3 oxidation state, while for Bi, +3 oxidation state is more stable than +5 oxidation state.

P, As, Sb } +5 state is more stable than +3 state

Bi } +3 state is more stable than +5 state

(1) Group 15 Elements

Group 15 includes nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) . These elements are collectively called the elements of nitrogen family after the name of first member of the group. On moving top to bottom in group, metallic nature of these elements goes on increasing.

Increase of Metallic nature ↓

N, P } Non-metals

As, Sb } Metalloid

Bi } Metal

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Here, nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids while, bismuth is a typical metal.

All the elements of this group are polyatomic in nature. Nitrogen is a diatomic gas, while other members are solid at room temperature.

Occurrence-

Molecular nitrogen comprises 78% by volume of the atmosphere. In earth's crust, it occurs as sodium nitrate, $NaNO_3$ (called Chile salt petre) and potassium nitrate, KNO_3 (called Indian salt petre). It is one of the major constituent of proteins in plants and animals.

Phosphorus occurs in minerals of the apatite family, $Ca_9(PO_4)_6$. CaX_2 (where, X = F, Cl or OH) e.g., fluorapatite $Ca_9(PO_4)_6$. CaF_2. These are the main components of phosphate rocks. It is also an essential constituent of bones and is also present in milk and eggs as Phosphoproteins.

Arsenic, antimony and bismuth are found mainly as sulphide minerals.

The important atomic and physical properties of nitrogen family are as under-

(1) Electronic Configuration-

The general outer shell electronic configuration of these elements is ns^2, np^3. Here, *s* orbital is completely filled while, p- orbitals are half-filled. Thus, these elements have extra stable electronic configuration and therefore, have extra stability.

(2) Atomic and Ionic Radii

On moving top to bottom in group, atomic (covalent) and ionic radii goes on increasing. It is because of the addition of new shells one by one.

Here, a considerable increase in covalent radius is observed from N to P. But, it is very small from As to Bi. It is because of insignificant screening effect of intervening electrons of *d* and *f* orbitals in heavier elements.

(3) Ionization Enthalpy

Ionization enthalpy goes on decreasing on moving down the group. It is due to gradual increase in atomic size down the group.

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Due to extra stable half-filled electronic configuration of *p* orbitals and smaller atomic size, the ionization enthalpy of the group 15 elements is much greater than that of group 14 elements of the corresponding period.

Similarly, due to more stable half-filled electronic configuration of *p* orbitals, the ionization enthalpy of the elements of group 15 are found to be exceptionally higher than those of the elements group 16 of respective period. For example, the ionization enthalpy of nitrogen is found to be exceptionally higher than that of oxygen.

Q. Give the reason-

Ionization enthalpy of N is found to be exceptionally higher than that of O.

Ans. The electronic configuration of N and O are as under-

N (7) = $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$

O (8) = $1s^2$, $2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$

Here, in case of N, electron is removed from 2p sub-shell having more stable half-filled electronic configuration. Hence, it requires relatively more energy for the removal of electron. Thus, it has exceptionally higher value of its ionization enthalpy.

On the other hand, in case of O, electron is also removed from 2p orbital but it has neither half-filled nor full-filled electronic configuration. Hence, it requires relatively lesser energy for the removal of electron. Thus, it has relatively lesser value of its ionization enthalpy.

(4) Electronegativity

The electronegativity of different elements, in general, decreases down the group due to increase of atomic size. However, in the heavier elements, the difference is is relatively less pronounced.

- **Melting point increases upto arsenic and then decreases upto bismuth.**
- **Except nitrogen, all the elements show allotropy.**

(5) Oxidation states and trends in chemical reactivity

The most common oxidation states of the elements of nitrogen family are –3, +3 and +5.

The tendency to show –3 oxidation state decreases down the group due to increase of atomic size and metallic character. Last member of the group i.e. bismuth does not show –3 oxidation state.

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The stability of +5 oxidation state decreases down the group. BiF_5 is the only compound where Bi shows +5 oxidation state.

The stability of +3 oxidation state increases (due to inert pair effect) down the group. For Bi, +3 oxidation state is the most stable oxidation state.

Nitrogen exhibits -3 oxidation state in its hydride (NH_3) and halides (NCl_3 and NBr_3) except NF_3 where, its oxidation state is +3. Along with, +3 and +5 oxidation states, it also exhibits + 1, + 2 and + 4 oxidation states in its oxides. In hydrazoic acid (N_3H), the oxidation state of nitrogen is -1/3.

All the oxidation states of nitrogen tend to disproportionate in acidic solution from +1 to +4 oxidation states. For example,

$$\overset{+3}{3HNO_2} \rightarrow \overset{+5}{HNO_3} + H_2O + \overset{+2}{2NO}$$

Phosphorus exhibits -3 oxidation state in its hydride (PH_3). Along with, +3 and +5 oxidation states, it also shows +1 and +4 oxidation states in some of its oxo-acids.

All the intermediate oxidation states of phosphorus disproportionate into +5 and –3 oxidation states, both in acidic and alkaline solutions.

For arsenic, antimony and bismuth, +3 oxidation state becomes increasingly stable with respect to disproportionation.

(6) Covalency

In nitrogen only four orbitals (one *s* and three *p*) are available in valence shell for bonding. Hence, its maximum covalency is restricted to 4. Since, the heavier elements contain vacant *d* orbitals in their outermost shell, they can expand their covalence beyond 4.

Anomalous properties of nitrogen

Nitrogen differs in properties from the rest of the members of its group. It is because of following reasons-

(1) Small atomic size

(2) High electronegativity

(3) High ionisation enthalpy

(4) Non-availability of *d* orbitals in its valence shell.

Nitrogen has unique ability to form *pπ - pπ* multiple bonds with itself and with other elements having small size and high electronegativity such as C and O. Heavier elements of this group do not form *pπ - pπ* bonds as their

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atomic orbitals are so large and diffuse that they cannot have effective overlapping.

Thus, nitrogen exists as a diatomic molecule having a triple bond between the two atoms. Consequently, its bond enthalpy (941.4 kJ mol^{-1}) is very high. On the contrary, phosphorus, arsenic and antimony form single bonds as P–P, As–As and Sb–Sb, while bismuth forms metallic bonds in elemental state. However, the single N–N bond is weaker than the single P–P bond. It is because of high inter-electronic repulsion of the non-bonding electrons, due to the small bond length. As a result the catenation tendency is weaker in nitrogen.

Another factor which affects the chemistry of nitrogen is the absence of *d* orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form *dπ – pπ* bond as the heavier elements can e.g. $R_3P = O$ or $R_3P = CH_2$ (where, R = alkyl group). Phosphorus and arsenic can form *dπ – dπ* bond with transition metals, especially when the compounds of these elements such as $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

Hydrides of Nitrogen family

All the elements of Nitrogen family (Group 15) form hydrides of type EH_3 (where E = N, P, As, Sb or Bi).

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Ammonia	Phosphine	Arsine	Stibine	Bismuthine

All these hydrides are covalent and are gaseous in nature at room temperature. Except, NH_3 all these hydrides are poisonous. In these hydrides, central atom is sp^3 hybridized and contains in all four electron pairs in its valence shell of which three are bond pairs, while rest one is lone pair. Due to presence of a lone pair of electrons, all these hydrides have pyramidal geometry.

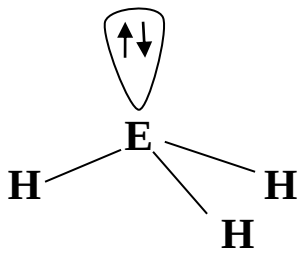


Fig.- Hydrides of N-family (Pyramidal)

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The important properties of the hydrides of N-family are listed here-

(1) Bond Angle

The bond angle of hydrides of N-family decreases on moving down the group and follows following order-

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

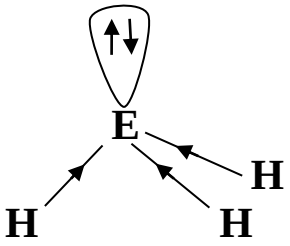


Fig.- Hydrides of N-family (Pyramidal)

In fact, bond angle of these hydrides depends upon the atomic size and electro-negativity of central atom. If the atomic size of central atom is smaller and its electro-negativity is larger, it attracts the bonded electron pair of E-H bond more strongly towards itself. Thus, distance between bonded electron pairs of E-H bonds gets decreased and therefore, repulsion amongst these electron pairs gets increased. Hence, the bond angle is relatively larger.

On moving down the group, the atomic size of central atom goes on increasing and electro-negativity goes on decreasing. Hence, the bond angle goes on decreasing.

Hydride	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Bond angle	107^0	94^0	92^0	91^0	-

(2) Thermal Stability

The thermal stability of hydrides of N-family decreases on moving down the group and follows following order-

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

In fact, on moving down the group, the atomic size of central atom goes on increasing and therefore, their bond dissociation enthalpy and thermal stability goes on decreasing.

Hydride	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Bond dissociation Enthalpy ($KJmol^{-1}$)	389	322	207	255	-

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(3) Reducing Nature

The reducing nature of hydrides of N-family increases on moving down the group and follows following order-

$$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$$

In fact, reducing nature of the hydrides depends upon their thermal stability and increases with decreases of thermal stability. On moving down the group, the atomic size of central atom goes on increasing and therefore, their bond dissociation enthalpy and thermal stability goes on decreasing. Hence, the reducing character of the hydrides goes on increasing. Here, ammonia shows mild reducing behavior, while BiH_3 is the strongest reducing agent amongst all the hydrides of N-family.

(4) Basic Nature

Basic strength of hydrides of N-family depends upon the availability of their lone pair of electrons for protonation. The greater the availability of their lone pair for protonation, more is basic strength of the respective hydride.

The basic strength of hydrides of N-family decreases on moving down the group and follows following order-

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

(5) Boiling point

In general, boiling point increases with increase of the molecular mass of the compounds. Hence, the boiling point of the hydrides of nitrogen family goes on increasing on moving down the group. However, the boiling point of NH_3 is found exceptionally higher than the boiling point of phosphine and arsine.

In fact, NH_3 involves intermolecular hydrogen bonding. Hence, additional intermolecular attraction operates amongst NH_3 molecules and its boiling point becomes exceptionally higher than that of phosphine and arsine.

Thus, the order of boiling point of different hydrides of N-family will be as under-

$$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$$

Hydride	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Boiling point (K)	238.5	185.5	210.6	254.6	290.0

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Ammonia (NH_3) -

Manufacture (Haber's process) -

On commercial scale, ammonia is manufactured by Haber's process. Here, nitrogen is reacted with hydrogen in presence of iron oxide with small amounts of K_2O and Al_2O_3 acting as catalyst at about 700 K temperature and about 200×10^5 Pa (about 200 atm) pressure to form ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 46.1 \text{ kJ mol}^{-1}$$

$$\Delta_f H^0 = -46.1 \text{ kJ mol}^{-1}$$

This reaction is reversible and exothermic and involves decrease in volume. Hence, according to Le Chatelier's principle, Low temperature and High pressure would be favourable for the formation of more ammonia. However, this temperature cannot be below 700 K because below this temperature the catalytic activity of catalyst gets highly reduced.

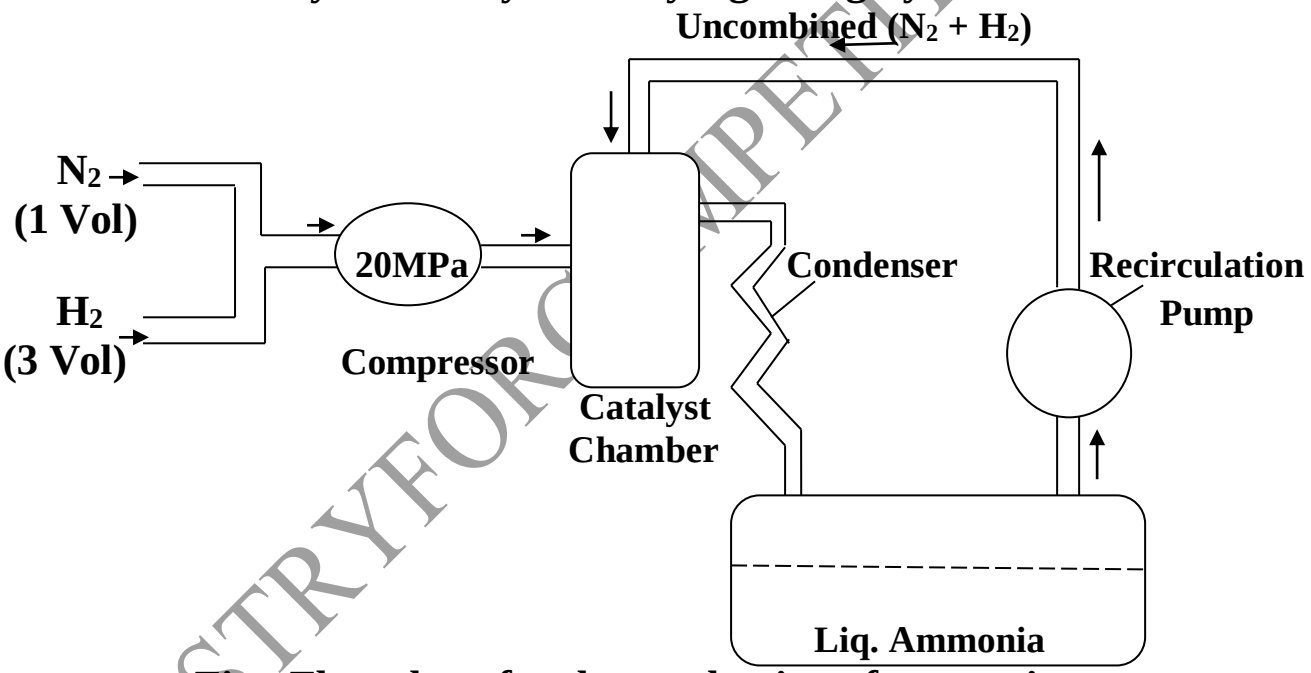


Fig.- Flow chart for the production of ammonia

- **Earlier, iron (Fe) was used as a catalyst with molybdenum (Mo) as a promoter in Haber's process.**
- **Ammonia is present in small quantities in air and soil, where it is formed by decay of nitrogenous organic matter e.g., urea.**

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

- **In a small scale, ammonia is obtained by decomposition of ammonium salts by action of caustic soda or calcium hydroxide.**

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

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

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Properties -

(1) Ammonia is a colourless gas with a pungent odour.

(2) Its freezing and boiling points are 198.4 and 239.7 K respectively.

(3) In solid and liquid states, it remains associated through intermolecular hydrogen bonds. It accounts for its higher melting and boiling points than expected on the basis of its molecular mass.

(4) Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the presence of OH^- ions in solution.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

(5) It forms ammonium salts with acids, e.g. NH_4Cl, $(NH_4)_2SO_4$ etc.

(6) Being a weak base, it precipitates the hydroxides (hydrated oxides in some cases) of many metals from their salt solutions. For example,

$$FeCl_3(aq) + 3NH_4OH(aq) \rightarrow Fe_2O_3.xH_2O(s) + 3NH_4Cl(aq)$$
(Brown ppt)

$$ZnSO_4(aq) + 2NH_4OH(aq) \rightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$$
(White ppt)

(7) Due to the presence of a lone pair of electrons on the central nitrogen Atom, the ammonia molecule behaves like a Lewis base and coordinate with metal ions to form complexes, which find applications in detection of metal ions such as Cu^{2+}, Ag^+ etc.

$$Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$$
(Blue) (Deep blue)

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$
(Colourless) (White ppt)

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]Cl(aq)$$
(White ppt) (Colourless)

Uses of Ammonia -

(1) In manufacture of nitrogenous fertilizers such as Urea, Ammonium nitrate, Ammonium sulphate, Ammonium phosphate etc.

(2) In manufacture of Nitric acid (HNO_3).

(3) As refrigerant.

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Structure -

Ammonia molecule has trigonal pyramidal geometry with nitrogen atom at the apex. Here, N-atom is sp^3 hybridized and contains in all four electron pairs in its valence shell of which three are bond pairs while, the rest one is lone pair. Here, the bond angle is 107^0.

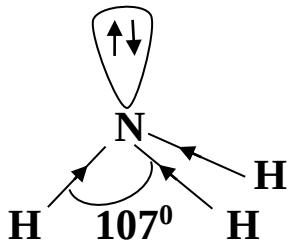


Fig.- Ammonia molecule (Pyramidal)

Q. Why does NH_3 act as a Lewis base ?

Ans- In NH_3 central Nitrogen atom contains a lone pair of electrons which is available for donation to other substances. Hence, it behaves like a Lewis base.

Oxides of N- Family -

All these elements, in general form following two types of oxides-

(1) E_2O_3 type

(2) E_2O_5 type

Here, the oxide having higher oxidation state of the element is more acidic than that having lower oxidation state.

The acidic character of oxides decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, those of arsenic and antimony are amphoteric and that of bismuth is predominantly basic. Thus, the order of acidic strength of the oxides of N-family will be as under-

$$\underbrace{N_2O_3 > P_2O_3}_{\text{Acidic}} > \underbrace{As_2O_3 > Sb_2O_3}_{\text{amphoteric}} > \underbrace{Bi_2O_3}_{\text{Basic}}$$

$$\underbrace{N_2O_5 > P_2O_5}_{\text{Acidic}}$$

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Oxides of Nitrogen-

Nitrogen combines directly or indirectly with oxygen to form following five oxides-

N_2O N_2O_2 or NO N_2O_3 N_2O_4 or NO_2 N_2O_5

Here, N_2O and NO are colourless gases while, NO_2 is a brown coloured gas at room temperature. N_2O_3 is a blue coloured solid and is stable only at low temperature while, N_2O_5 is a colourless solid at room temperature. Amongst these oxides, N_2O and NO are neutral oxides, while all other oxides are acidic in nature. Acidic nature of these oxides goes on increasing with increase of the oxidation state of nitrogen atom in respective oxide. Thus, the order of acidic strength of different oxides of nitrogen will be as under-

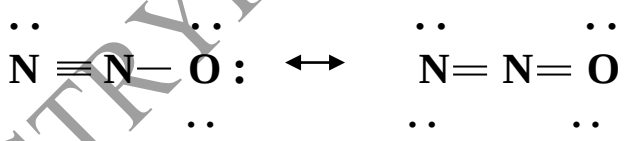
$$N_2O_3 < NO_2 < N_2O_5$$

(1) Nitrous oxide or Nitrogen (I) oxide (N_2O)- It is a colouress gas which is prepared by thermal decomposition of ammonium nitrate.

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

It produces hysterical laughing, if inhaled. Hence, it is also called laughing gas. It is also used as local anaesthetic in dental surgery.

N_2O is linear in geometry and is considered to be resonance hybrid of following two resonance structures.



(2) Nitric oxide or Nitrogen (II) oxide (NO)- It is a colouress gas which is produced by reduction of sodium nitrite with ferrous sulphate in presence of sulphuric acid.

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \xrightarrow{\Delta} Fe_2(SO_4)_3 + 2NaHSO_4 + 2NO + 2H_2O$$

It is an odd electron molecule which contains an unpaired electron. Hence, it is attracted in magnetic field and is paramagnetic in nature.

It readily undergoes dimerization where its unpaired electron gets paired up. Thus, its dimer (N_2O_2) is diamagnetic in nature.

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NO is considered to be resonance hybrid of following two resonance structures.

$$:\dot{N} = \ddot{O}: \quad \leftrightarrow \quad :\dot{N} = \dot{O}:$$

- **NO is absorbed in Ferrous sulphate.**
- **In ring test of nitrate ions, brown ring of nitroso ferrous sulphate, $[Fe(H_2O)_5NO]SO_4$ is formed. In this complex iron appears to be in +2 oxidation state. However, its magnetic moment reveals that, in this compound iron is present in +1 oxidation state. Here, NO also exhibit +1 oxidation state.**

(3) Dinitrogen trioxide or Nitrogen (III) oxide (N_2O_3)- It is a blue coloured solid which is obtained by cooling a mixture of nitric oxide and nitrogen dioxide up to about 250K temperature.

$$NO + NO_2 \xrightarrow{250K} N_2O_3$$

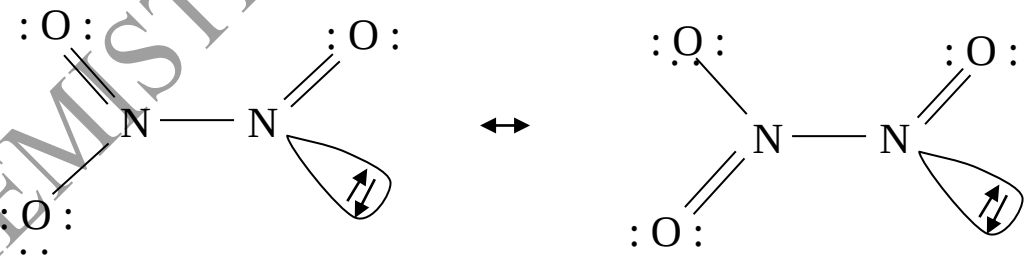
It is also called nitrogen sesquioxide. It is an acidic oxide and is also called anhydride of nitrous acid.

$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

(Nitrous acid)

It is an unstable oxide which gets decomposed into NO and NO_2 on rise of temperature.

This molecule has planar geometry and is considered to be resonance hybrid of following two resonance structures.



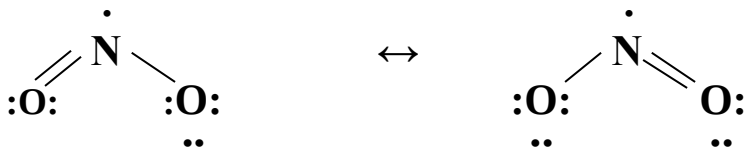
(4) Nitrogen dioxide or Nitrogen (IV) oxide (NO_2)- It is a brown coloured gas which is produced by thermal decomposition of lead nitrate.

$$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$$

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It is also an odd electron molecule which contains an unpaired electron. Hence, it is attracted in magnetic field and is paramagnetic in nature.

NO_2 is considered to be resonance hybrid of following two resonance structures.



In NO_2 central nitrogen atom is sp^2 hybridized. It has V-shaped (bent) geometry.

It readily undergoes dimerization, where its unpaired electron gets paired up. Thus, its dimer (N_2O_4) is diamagnetic in nature.

$$2NO_2 \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} N_2O_4$$

Brown colourlesss liquid/solid

- **Brown coloured gas coming out from fuming nitric acid is NO_2.**
- **N_2O_4 molecule has planar geometry where, all the atoms lie in same plane.**

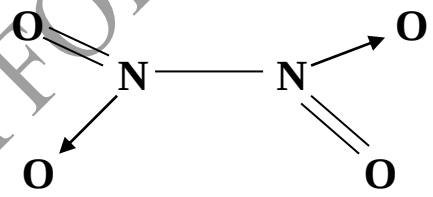


Fig.- Geometry of N_2O_4 molecule (Planar)

- **N_2O_4 is considered to be mixed anhydride of Nitrous acid (HNO_2) and nitric acid (HNO_3).**

(5) Dinitrogen pentoxide or Nitrogen (V) oxide (N_2O_5)- It is a colouress solid and is prepared by action of concentrated nitric acid on phosphorus pentoxide.

$$P_2O_5 + 4HNO_3 \xrightarrow{\Delta} 2N_2O_5 + 4HPO_3$$

It is the most acidic oxide of nitrogen. It also has planar geometry where, bond angle of N-O-N bond is 112^0.

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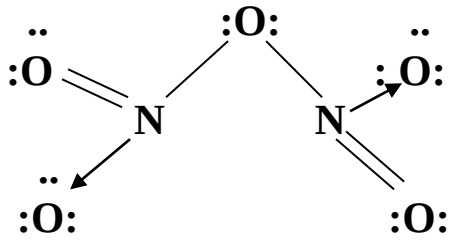


Fig.- Geometry of N_2O_5 molecule (Non-planar)

- **X-ray studies have revealed that solid N_2O_5 is ionic in nature and exist as $NO_2^+NO_3^-$ i.e. as nitronium nitrate.**
- **It is considered to be anhydride of nitric acid (HNO_3).**

Q. What is the covalence of nitrogen in N_2O_5 ?

Q. Why does NO_2 dimerise ?

Ans- NO_2 contains odd number of valence electrons and therefore, it behaves like a typical Odd electron molecule. On dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons. Hence, it undergoes dimerization readily.

Q. Give the reason- Though nitrogen exhibits +5 oxidation state, it does not form pentahalide.

Ans.- In Nitrogen second shell is the outermost shell, which contains only *s* and *p* orbitals. It does not contain *d*-orbitals in its valence shell and therefore cannot expand its covalence beyond four. It is the reason why it does not form pentahalides.

Q. PH_3 has lower boiling point than NH_3. Why?

Ans.- Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

Halides of Nitrogen Family-

These elements react with halogens to form following two series of halides-

(1) EX_3 series

(2) EX_5 series

Nitrogen does not form pentahalides due to non-availability of the *d* - orbitals in its valence shell. Pentahalides are more covalent than trihalides.

All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF3 are predominantly covalent in nature.

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Reactivity towards metals-

All these elements react with metals to form their binary compounds where, they exhibit the oxidation state of –3. For example, Ca_3N_2 (calcium nitride), Ca_3P_2 (calcium phosphide), Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide), Mg_3Bi_2 (magnesium bismuthide) etc.

Q. Why are pentahalides more covalent than trihalides ?

Q. Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements ?

Oxo Acids of Nitrogen

Nitrogen forms a number of oxo-acids of which most common are as under-

(1) Hyponitrous acid ($H_2N_2O_2$)

(2) Nitrous acid (HNO_2)

(3) Nitric acid (HNO_3)

Amongst these oxo acids HNO_3 is the most important.

Nitric Acid (HNO_3)-

Preparation Methods –

(1) Laboratory Preparation

In the laboratory, nitric acid is prepared by heating $NaNO_3$ or KNO_3 with concentrated H_2SO_4 in a glass retort.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

(2) COMMERCIAL PREPARATION –

(Ostwald's process)

On a large scale nitric acid is prepared mainly by Ostwald's process. This method involves catalytic oxidation of NH_3 by atmospheric oxygen in presence of Pt /Rh gauge acting as catalyst at about 500K temperature and 2-9 bar pressure to get nitric oxide.

$$4NH_3\,(g) + 5O_2\,(g) \rightarrow 4NO\,(g) + 6H_2O\,(g)$$

Nitric oxide thus formed combines with oxygen giving NO_2.

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$$

Nitrogen dioxide so formed, dissolves in water to give HNO_3.

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$$3NO_2\,(g) + H_2O \rightarrow 2HNO_3\,(aq) + NO\,(g)$$

Aqueous HNO_3 thus obtained is concentrated by distillation where, about 68% acid by mass is obtained. Further concentration is carried out by dehydration with concentrated H_2SO_4 where, 98% concentrated acid is obtained.

NO formed in this method is recycled to get more HNO_3.

Physical Properties

(1) It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K).

(2) Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.

(3) Nitric acid behaves like a strong acid and ionizes almost completely in its aqueous solution to give hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

Chemical Properties

Reaction with Nonmetals-

(1) Reaction with Carbon-

Conc. and hot nitric acid oxidizes carbon into carbon dioxide.

$$[2HNO_3 \rightarrow 2NO_2 + H_2O + [O]\ ] \times 2$$
$$C + 2[O] \rightarrow CO_2$$

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

(2) Reaction with Iodine-

Conc. and hot nitric acid oxidizes iodine into iodic acid.

$$[2HNO_3 \rightarrow 2NO_2 + H_2O + [O]\ ] \times 5$$
$$I_2 + 5[O] \rightarrow I_2O_5$$
$$I_2O_5 + H_2O \rightarrow 2\,HIO_3$$

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

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(3) Reaction with Sulphur-

Conc. and hot nitric acid oxidizes sulphur into sulphuric acid.

$$[2HNO_3 \rightarrow 2NO_2 + H_2O + [O]\ ] \times 24$$
$$S_8 + 16[O] \rightarrow 8SO_2$$
$$[SO_2 + H_2O + [O] \rightarrow H_2SO_4] \times 8$$

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

(4) Reaction with Phosphorus-

Conc. and hot nitric acid oxidizes phosphorus into phosphoric acid.

$$[2HNO_3 \rightarrow 2NO_2 + H_2O + [O]\ ] \times 10$$
$$P_4 + 10[O] \rightarrow 2P_2O_5$$
$$[P_2O_5 + 3H_2O \rightarrow 2H_3PO_4] \times 2$$

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

Reaction with Metals

Concentrated HNO_3 acts like a strong acid as well as a strong oxidising agent. It attacks most metals except noble metals such as gold and platinum. Here, the oxidation products depend upon following factors-

(1) Concentration of the acid
(2) Nature of the metal
(3) Position of metal in electro chemical series
(4) Temperature

Reaction of nitric acid with some most common metals are as under-

(1) Reaction with Zinc –

(a) Dilute and cold nitric acid oxidizes zinc into zinc nitrate and releases nitrous oxide.

$$2HNO_3 \rightarrow N_2O + H_2O + 4[O]$$
$$[Zn + 2HNO_3 + [O] \rightarrow Zn(NO_3)_2 + H_2O\ ] \times 4$$

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

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(b) Conc. and hot nitric acid oxidizes zinc into zinc nitrate and releases nitrogen dioxide.

$$2HNO_3 \rightarrow 2NO_2 + H_2O + [O]$$
$$Zn + 2HNO_3 + [O] \rightarrow Zn(NO_3)_2 + H_2O$$

$$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

(2) Reaction with Copper –

(a) Dilute and cold nitric acid oxidizes copper into cupric nitrate and releases nitric oxide.

$$[Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2[H]\ ] \times 3$$
$$[HNO_3 + 3[H] \rightarrow NO + 2H_2O] \times 2$$

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

(b) Conc. and hot nitric acid oxidizes copper into cuppric nitrate and releases nitrogen dioxide.

$$Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2[H]$$
$$[HNO_3 + [H] \rightarrow NO_2 + H_2O] \times 2$$

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

- **Some metals like Cr, Al etc. do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.**

Brown Ring Test-

The familiar brown ring test for nitrates is due to the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex.

Here, dilute ferrous sulphate solution is added to an aqueous solution containing nitrate ion, and then concentrated sulphuric acid is added along the sides of the test tube where a brown ring is formed at the interface of the solution and sulphuric acid.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$
$$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$$
(brown)

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Structure-

In gaseous state, HNO_3 exists as a planar molecule with following Structure-

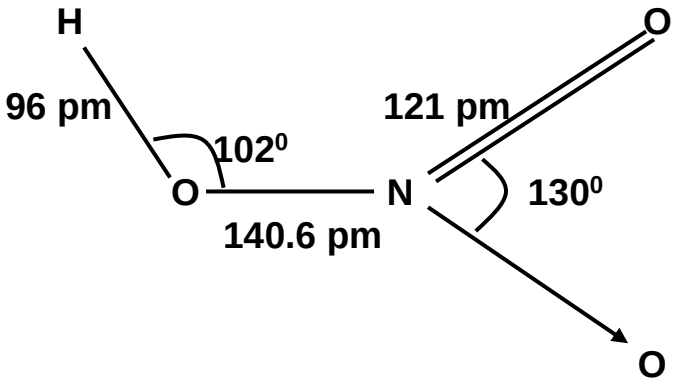


Fig.- Geometry of HNO_3 Molecule (Planar)

Uses of Nitric acid-

(1) In the manufacture of ammonium nitrate for fertilizers.
(2) In the manufacture of other nitrates for explosives and pyrotechnics.
(3) In preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds.
(4) In the pickling of stainless steel and etching of metals
(5) As an oxidizer in rocket fuels.

Allotropes of Phosphorus

Phosphorus is found in many allotropic forms of which the most common allotropes are as under-

(1) White phosphorus
(2) Red phosphorus
(3) Black phosphorus

(1) White phosphorus

(1) It is a white coloured, translucent, waxy solid which glows in dark i.e. shows chemiluminescence.
(2) It is insoluble in water but soluble in carbon disulphide.

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(3) It dissolves in boiling NaOH solution in an inert atmosphere to form phosphine (PH_3).

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

Sodium hypophosphite

(4) It is poisonous in nature and therefore it is used as rat poison.

(5) White phosphorus is less stable and therefore, more reactive than the other allotropes under ordinary conditions. It is because of large angular strain in the P_4 molecule due to very small bond angles(i,e. 60°).

(6) It readily catches fire in air to give dense white fumes of P_4O_{10}.

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

STRUCTURE- It contains discrete tetrahedral P_4 molecule.

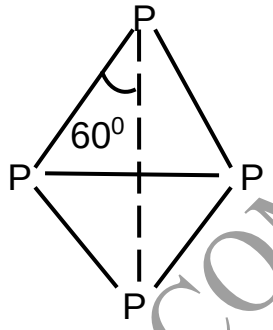


Fig. P_4 molecule of White phosphorus

(2) Red phosphorus –

(1) It is obtained by heating white phosphorus at 573K in an inert atmosphere for several days.

(2) When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed.

(3) Red phosphorus possesses iron grey lustre.

(4) It is odourless, nonpoisonous and insoluble in water as well as in carbon disulphide.

(5) Chemically, red phosphorus is much less reactive than white phosphorus.

(6) It does not glow in the dark.

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Structure-

Red phosphorus is polymeric and contains the chains of P_4 tetrahedra linked together in following manner-

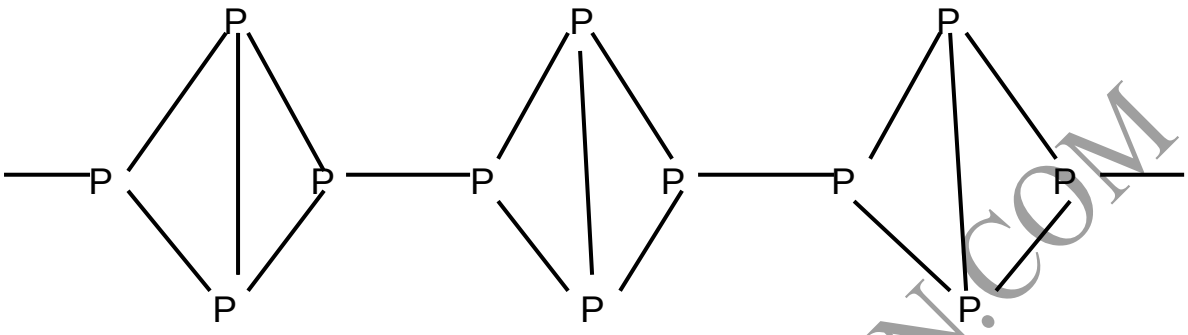


Fig.- Red Phosphorus

(3) Black phosphorus- It has following two forms –

(i) α-black phosphorus

(ii) β-black phosphorus

α-Black phosphorus is formed by heating red phosphorus in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidize in air.

β-Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

Oxoacids of Phosphorus

Phosphorus forms following two series of oxoacids-

(1) Phosphorus series

(2) Phosphoric series

In all these oxoacids, phosphorus atom is sp^3 hybridized and remains tetrahedrally surrounded by other atoms. These acids contain at least one P=O and one P-OH. Those oxoacids in which phosphorus has lower oxidation states also contain either P-H bonds or P-P bond but not both. Here, the hydrogen atoms of O-H group are ionizable and therefore, are acidic in nature. The number of such hydrogen atoms corresponds to the basicity of the acid. On the other hand, the hydrogen atoms attached directly to the phosphorus atom are non-ionizable and therefore, non-acidic in nature. These hydrogen atoms are responsible for the reducing nature of the acid.

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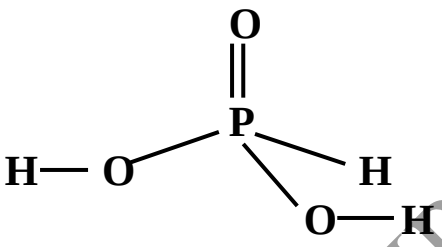
Oxoacids of Phosphorus involve pπ-dπ bonds between oxygen and phosphorus atoms.

Those oxoacids in which phosphorus has +3 oxidation state tend to disproportionate. For example, orthophosphorus acid disproportionate on heating to form orthophosphoric acid and phosphine.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

Some important oxoacids of Phosphorus along with their geometry and important properties are listed here-

(1) Ortho phosphorus acid or Phosphonic acid (H_3PO_3)



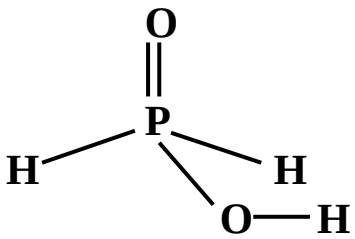
Ortho phosphorus acid
(P = +3)

It is a weak di-basic acid which ionizes in two steps and therefore, has two acidity constants.

$$H_3PO_3 \leftrightharpoons H^+ + H_2PO_3^-$$
$$H_2PO_3^- \leftrightharpoons H^+ + HPO_3^{2-}$$

It forms two types of salts of which one is acidic while, the other one is neutral. Here, since, one of the hydrogen atoms is directly attached to the phosphorus atom, it shows reducing behaviour.

(2) Hypophosphorus acid or Phosphinic acid (H_3PO_2)



Hypophosphorus acid
(P = +1)

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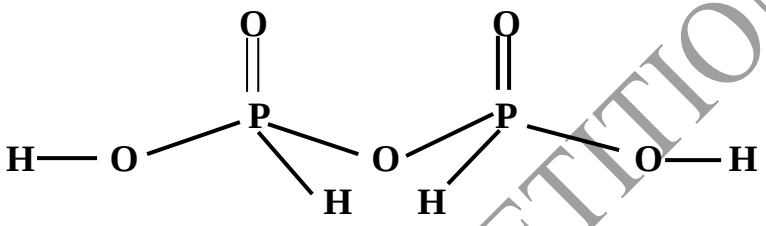
It is a weak mono-basic acid which ionizes in only one step and therefore, has only one acidity constant.

$$H_3PO_2 \rightleftharpoons H^+ + H_2PO_2^-$$

It forms only one type of salt, which is neutral. Here, since, two hydrogen atoms are directly attached to the phosphorus atom, it shows strong reducing behaviour. It reduces silver nitrate to metallic silver.

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

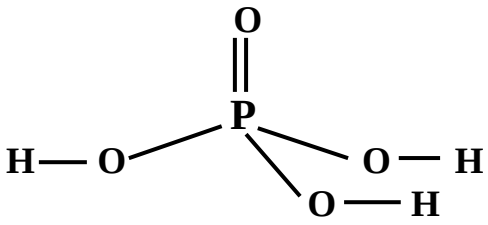
(3) Pyro Phosphorus acid ($H_4P_2O_5$)



Pyro phosphorus acid
(P = +3)

It is obtained by removal of a water molecule from two molecules of phosphorus acid. It is also a dibasic acid which shows weak reducing behaviour. It involves P-O-P bond.

(4) Orthophosphoric acid (H_3PO_4)

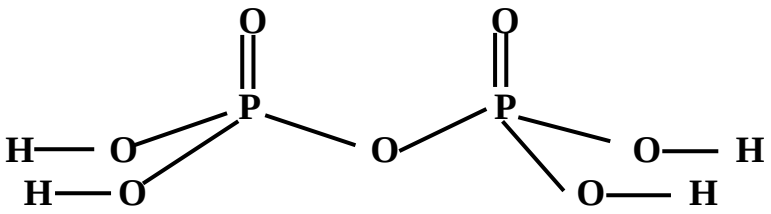


Orthophosphoric acid
(P = +5)

It is a tribasic moderate acid which shows weak oxidizing behaviour. It ionizes in three steps and therefore, has three acidity constants. It forms three types of salts of which two are acidic while, the rest one is neutral.

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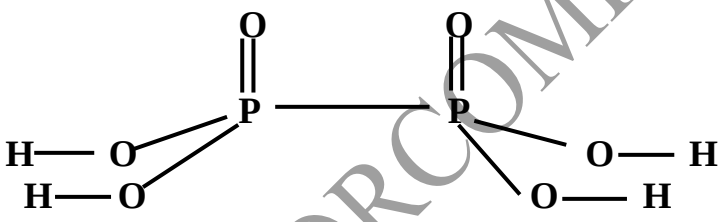
(5) Pyrophosphoric acid ($H_4P_2O_7$)



Pyrophosphoric acid
(P = +5)

It is obtained by removal of a water molecule from two molecules of phosphoric acid. It is a tetra-basic acid which also shows weak oxidizing behaviour. It involves P-O-P bond.

(6) Hypophosphoric acid ($H_4P_2O_6$)

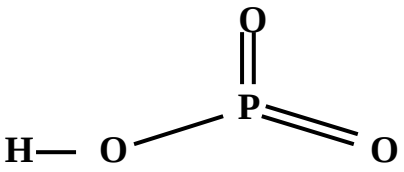


Hypophosphoric acid
(P = +4)

It is a tetra-basic acid which involves P - P bond. It is the only oxo-acid of phosphorus in which both the phosphorus atoms remain bonded together directly.

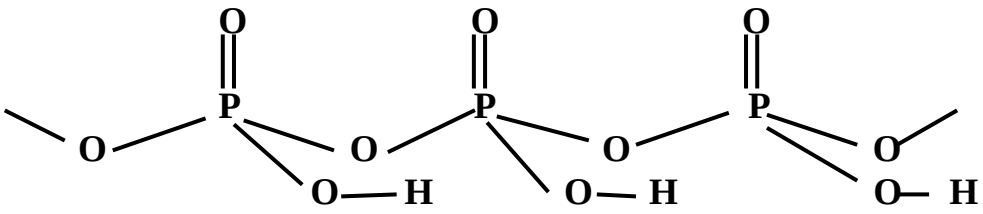
(7) Metaphosphoric acid $(HPO_3)_n$-

It is the the only oxo acid of phosphorus which exists in polymeric open chain or cyclic forms. Its monomeric form is as under-

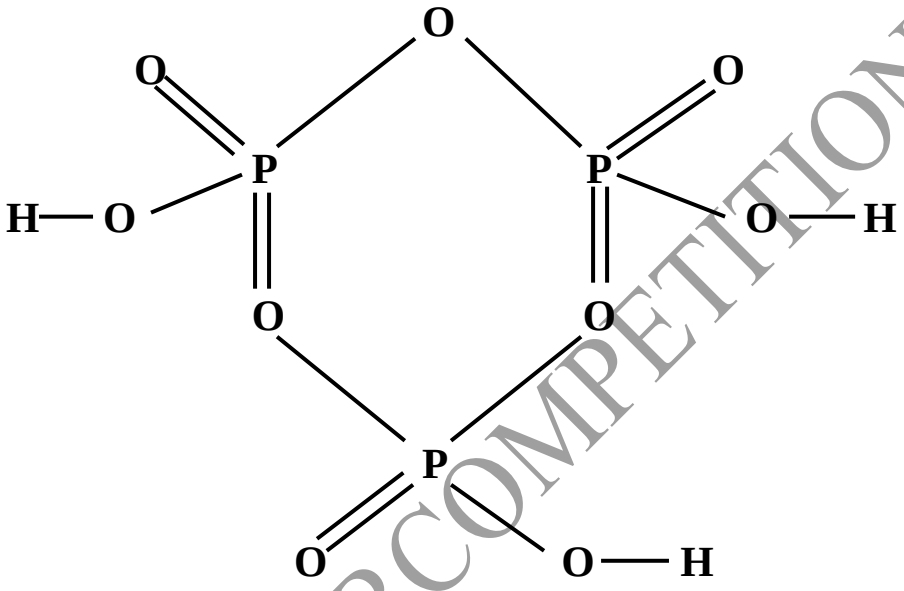


Monomer of metaphosphoric acid
(P = +5)

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Polymetaphosphoric acid, $(HPO_3)_n$
(Open chain form)
(P = +5)



Cyclotrimetaphosphoric acid $(HPO_3)_3$
(P = +5)

Phosphine (PH_3)

Preparation Methods-

(1) By action of water or dilute HCl on calcium phosphide

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$
$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$$

(2) In the laboratory, phosphine is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + Na_2HPO_2$$

Sodium hypophosphite

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In pure form it is non inflammable but becomes inflammable in presence of P_2H_4 or P_4 vapours. For purification it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH releases phosphine.

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

Properties

(1) It is a colourless gas with rotten fish smell and is highly poisonous.

(2) It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

(3) It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

(4) When absorbed in copper sulphate or mercuric chloride solution, the Corresponding phosphides are obtained.

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

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

(5) Phosphine is weakly basic in nature. Just like ammonia, it reacts with acids to form phosphonium compounds. For example,

$$PH_3 + 4HBr \rightarrow PH_4Br$$

Uses- The spontaneous combustion of phosphine is technically used in *Holme's signals*. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal. It is also used in *smoke screens*.

Q.-In what way can it be proved that PH_3 is basic in nature?

Ans.- PH_3 reacts with acids like HI to form PH_4I which shows that it is basic in nature.

$$PH_3 + HI \rightarrow PH_4I$$

In fact, due to presence of a lone pair of electrons on phosphorus atom, PH_3 acts like a Lewis base.

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Phosphorus Trichloride (PCl_3)

Phosphorus forms two types of halides, PX_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br) type.

Preparation-

(1) By passing dry chlorine over heated white phosphorus.

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

(2) By action of thionyl chloride on white phosphorus.

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

Properties

(1) It is a colourless oily liquid and hydrolyses in the presence of moisture.

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

(2) It reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH.

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

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

Structure-

In PCl_3 central phosphorus atom is sp^3 hybridized and contains in all four electron pairs in its valence shell of which three are bond pairs while, rest one is lone pair. Due to presence of a lone pair of electrons it has pyramidal geometry.

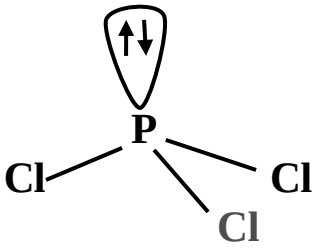


Fig.- Geometry of PCl_3 (Pyramidal)

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Phosphorus Pentachloride (PCl_5)

Preparation

(1) By the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

(2) By the action of SO_2Cl_2 on phosphorus.

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

Properties

(1) It is a yellowish white powder.

(2) In moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

(3) On heating it sublimes. However, it decomposes on stronger heating to form PCl_3 and Cl_2.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

(4) It reacts with organic compounds containing –OH group to convert them to the chloro derivatives.

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$
$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

(5) When finely divided metals are heated with PCl_5 they form their corresponding chlorides.

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

Uses-

It is used in the synthesis of some organic compounds, such as C_2H_5Cl, CH_3COCl.

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Structure

In PCl_5 central phosphorus atom is sp^3d hybridized. Hence, in gaseous and liquid phases, it has trigonal bipyramidal geometry.

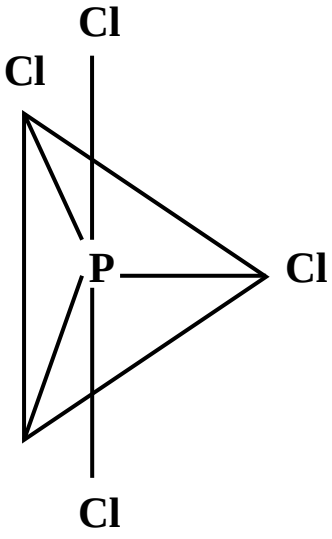


Fig.- Geometry of PCl_5 molecule (trigonal bipyramidal)

Here, three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that, the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.

In the solid state it exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ is octahedral.

Q. Why does PCl_3 fume in moisture ?

Ans.- In presence of moisture PCl_3 hydrolyses to give the fumes of HCl(g).

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

Q.- Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

Ans.- PCl_5 has trigonal bipyramidal geometry where, three equatorial P-Cl bonds are equivalent, while the rest two axial bonds are different and longer than equatorial bonds.

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