DAV CENTENARY PUBLIC SCHOOL

PASCHIM ENCLAVE

GROUP – 15 ELEMENTS

Q1. Why is it that molecular nitrogen is not particularly reactive?

Ans. Molecular nitrogen is inert due to the presence of triple bond between two nitrogen atoms. Because of this triple bond, bond energy is very high.

Q2. A nitrogen atom posseses five valence electrons, but it does not form the compound of the type NCl_5. Give reason.

Ans. Yes, A nitrogen atom posseses five valence electrons, but it does not form the compound of the type NCl_5, because nitrogen atom has no vacant d – orbitals to expand its octet.

Q3. What is the difference between the nature of pi – bonds present in H_3PO_3 and HNO_3 molecules?

Ans. In HNO_3 there is p π - p π bonding and in H_3PO_3 there is p π-d π bonding.

Q4. How is the nature of pi bonding in H_3PO_4 different from that in HNO_3?

Ans. In HNO_3 p π - p π forms multiple bonding whereas in H_3PO_4 there is no p π - p π multiple bonding.

Q5. Write the reaction between red lead (Pb_3O_4) and dilute HNO_3?

Ans. $Pb_3O_4 + HNO_3 \rightarrow Pb(NO_3)_2 + PbO_2 + 2H_2O$

Q6. Explain why phosphorus forms PF_5, whereas nitrogen does not form NF_5?

Ans. Phosphorus can form PF_5 as phosphorus has got vacant d – orbitals in its valence shell and phosphorus can expand its d – orbitals whereas nitrogen cannot form NF_5 as nitrogen does not have vacant d – orbitals to expand

Q7. Complete the following reaction

$Ca_3P_2 + H_2O \rightarrow$ ---------- + $Ca(OH)_2$

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

Q8. Write the balanced chemical reaction for the preparation of hydrazine (N_2H_4).

Ans. $2NH_3 + NaOCl \rightarrow N_2H_4 + NaCl + H_2O$

Q9. Which one of the hydrides of 15th group is soluble in water and why?

Ans. Ammonia is soluble in water because it forms hydrogen bond with water. Other hydrides do not form hydrogen bonding with water.

Q10. On being slowly passed through water PH_3 forms bubbles but NH_3 dissolves. Why is it so?

Ans. NH_3 form intermolecular H-bonding with water while PH_3 can't.

Q11. Write the products formed when ammonium nitrate is heated.

Ans. $NH_4NO_3 \rightarrow N_2O + 2H_2O$

Q12. Write the products formed when lead nitrate is heated.

Ans. $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$

Q13. Write the balanced equation for the preparation of NO.

Ans. $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$

Q14. Which of the following is a tri – basic acid?

H_3PO_3 and H_3PO_4

Ans. Try yourself. (Hint : draw the structure then on the basis of no. of -OH bond attached basicity decided.)

Q15. Wtire the structure of cyclotri – metaphosphoric acid.

Ans. Try yourself.

Q16. Write the structure of pyrophosphoric acid ($H_4P_2O_7$).
Ans. Try yourself.

Q17. NO_2 is coloured but the dimmer N_2O_4 is colourless. Explain.
Ans. NO_2 is coloured because of the presence of unpaired electrons, whereas N_2O_4 is colourless because of the absence of unpaired electrons in its d – orbitals.

Q18. What is the hybridization of nitrogen in NO_3^- ion?
Ans. sp^2.

Q19. Which of the following is more covalent : $SbCl_5$ or $SbCl_3$?
Ans. $SbCl_5$, because in $SbCl_5$ the oxidation state of Sb is +5 and covalent characters are increased with the increase in oxidation state (Fazan's Rule).

Q20. Why PH_3 is weaker base than NH_3?
Ans. The size of P is larger than the size of N, hence the lone pair of electron (which is responsible for basic characters) is distributed on large area in P than N. Therefore, the tendency to donate the lone pair is less in PH_3 than in NH_3.

Q21. Why H_3PO_3 is diprotic?
Ans. This is due to because out of the three hydrogens, one is directly attached to the phosphorus, which cannot be ionized. Only two hydrogens attached to the oxygens, give two H^+ ions hence it is diprotic.

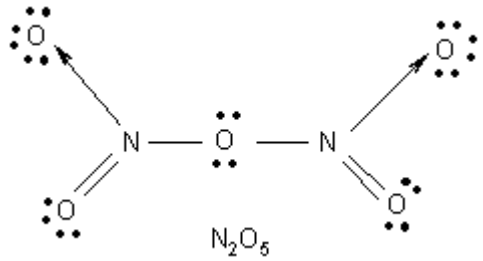
Q22. Draw the structure of AsH_3, PH_3, and PF_5 in gas phase.
Ans. Try yourself. (hint: draw according to VSEPR THEORY)

Q23. Draw the molecular structures of two oxoacids of phosphorus other than orthophosphoric acid.
Ans. Try yourself.

Q24. Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.
Ans. PCl_5 has a trigonal bipyramidal structure and the three equatorial P – Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds. This is because axial pairs in this arrangement experience relatively larger repulsive interactions. Hence axial bonds are relatively longer than equatorial bonds.

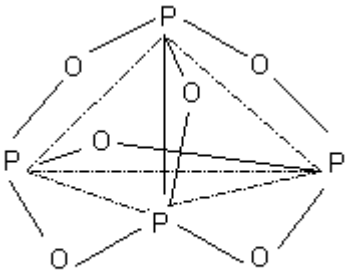
Q25. Explain why nitrogen forms a large no. of oxides than phosphorus.
Ans. Due to ability of the nitrogen to form p π - p π multiple bonds, nitrogen forms a larger no. of oxides, whereas phosphorus does not have the ability to form p π - p π bonds hence it does not give larger no. of oxides.

Q26. Oxides of nitrogen have open chain structures while those of phosphorus have closed chain or cage structures. Why is it so? Illustrate with one structural example for each type of oxides.
Ans. Due to ability of nitrogen to form p π - p π multiple bonds, the oxides of nitrogen have open chain structure.

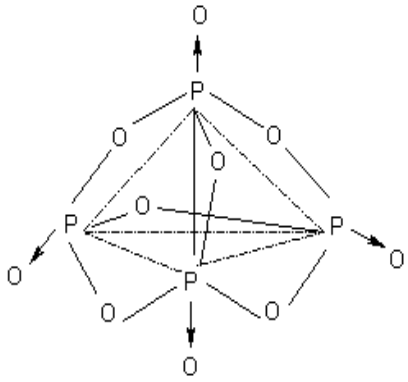


N_2O_5

Due to reluctance of phosphorus to form p π - p π multiple bonds due to the large size of P as compared to N, their oxides have cage structures.



P_4O_6



P_4O_{10}

Q27. Explain why nitrogen exists as a diatomic molecule, N_2, whereas phosphorus exists as tetratomic molecule.

Ans. The existence of nitrogen as diatomic molecules is due to its ability to form p π - p π multiple bonds which is not possible in the case of phosphorus due to repulsion between non – bonded electrons of the inner core.

Q28. What is responsible for the blue colour of a solution of an alkali metal in liquid ammonia?

Ans. In liquid ammonia, alkali metal atom loses electron which combines with ammonia to produce blue ammonia solvated electron.

Q29. On being slowly passed through water PH_3 forms bubbles but NH_3 dissoves. Why is it so?

Ans. Ammonia can form hydrogen bonding with water, hence it is soluble in water but PH_3 cannot form hydrogen bond with water, hence it form bubbles when passes through the water.

Q30. What are the oxidation state shown by antimony?

Ans. +3 and +5.

Q31. Nitrogen does not form any pentahalide like phosphorus. Why?

Ans. Nitrogen does not form any pentahalide because it cannot expand its octet due to the non availability of d orbitals but phosphorus can expand its octer because of the availability of d orbitals, hence can form pentahalide.

Q32. Give the disproportionation of H_3PO_3.

Ans. On heating H_3PO_3 disproportionates to give phosphoric acid and phosphine.

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

Q33. Why does NO_2 dimerises? Explain.

Ans. NO_2 contains odd number of valence electrons. It behaves as a typical molecule. In the liquid and solid state, it dimerises to form stable N_2O_4 molecule, with even number of electrons. Therefore, NO_2 is paramagnetic, while N_2O_4 is diamagnetic in which two unpaired electrons get paired.

Q34. Unlike phosphorus nitrogen shows little tendency for catenation. Explain.

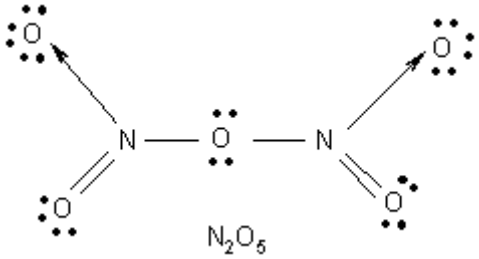
Ans. Nitrogen has little tendency for catenation because N – N single bond is weak. This is because nitrogen has small size and the lone pairs on two nitrogen atoms repel each other. On the other hand, phosphorus is comparatively large in size so that lone pairs on P atoms do not repel to the same extent. As a result P – P bond is stronger than N – N bond. Therefore, P has a tendency for catenation because of high bond enthalpy of P – P bond.

Q35. Bismuth is a strong oxidizing agent in pentavalent state.

Ans. In Bismuth +3 oxidation state is more stable than +5 state because of inert pair effect of 6s electrons. Therefore, +5 oxidation state can be changed to +3 oxidation state easily and bismuth acts as a strong oxidizing agent due to this change in oxidation state.

Q36. What is the covalence of nitrogen in N_2O_5.

Ans. N_2O_5 has the structure



The covalence of nitrogen in the above structure is four because it has four shared pair of electrons.

Q37. In what way it can be proved that PH_3 is basic in nature.

Ans. PH_3 reacts with acids like HI to form phosphonium iodide, PH_4I.

$$PH_3 + HI \rightarrow PH_4I$$

This shows that PH_3 is basic in nature. This basic nature of PH_3 is due to the presence of lone pair on phosphorus atom and therefore, it acts as a Lewis base.

Q38. Why does PCl_3 fume in moisture?

Ans. PCl_3 gets hydrolysed in the presence of moisture and gives fumes of HCl.

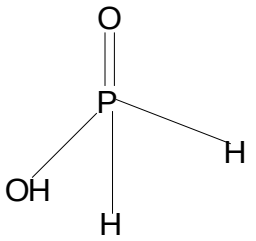
$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

Q39. All the five bonds in PCl_5 are not equivalent. Justify.

Ans. PCl_5 has trigonal bipyramidal structure in which there are three P – Cl equatiorial bonds and two P – Cl axial bonds. The two axial bonds are being repelled by three bond pairs at 90^0. Therefore, axial bonds are repelled more by bond pairs than equatorial bonds and hence are larger than equatorial bonds.

Q40. How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure.

Ans.



Since two H atoms are bonded directly to P atom which impart reducing character to the acid.

Q41. What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2.

Ans. Phosphine is formed.

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

Q42. What happens when PCl_5 is heated?

Ans. On heating, PCl_5 first sublimes and then decomposes on strong heating.

$$PCl_5 \rightarrow PCl_3 + Cl_2$$

Q43. Write the short note on allotropic forms of phosphorus,.

Ans. Phosphorus is found in many allotropic foms, the important ones being white, red and black.

WHITE PHOSPHORUS : - It is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark **(chemiluminescence)**. It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3.

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

White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule where the angles are only 60^0. It readily catches fire in air to give dense white fumes of P_4O_{10}.

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

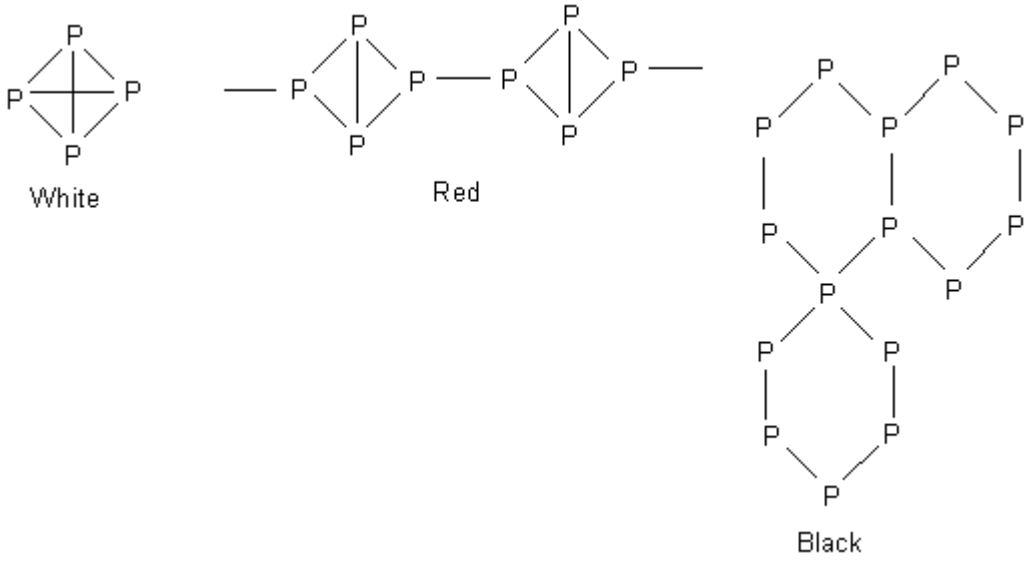
It consists of discrete tetrahedral P_4 molecule.

RED PHOSPHORUS:- It is obtained by heating white phosphorus at 573 K in an inert atmosphere for several days.

When red phosphorus is heater under high pressure, a series of phases of black phosphorus are formed.

Red phosphorus possesses iron grey lustre. It is odourless, non toxic and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark. It is polymeric consisting of chains of P_4 tetrahedra linked together in the manner.

BLACK PHOSPHORUS : - It has two forms α – black phosphorus and β – black phosphorus. α – black phosphorusis formed when red phosphorus is heated in a sealed tube at 803 K. 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.



Q44. What happens when orthophosphorous acid is heated?

Ans. On heating, H_3PO_3 disproportionates to give phosphoric acid and phosphine.

$$4\ H_3PO_3 \rightarrow 3\ H_3PO_4 + PH_3$$
$$+3 \qquad +5 \quad -3$$

Q45. Nitric oxide becomes brown when released in air.

Ans. When nitric oxide, NO is released in air, it becomes brown due to the formation of NO_2, which is a brown gas. $2NO + O_2 \rightarrow 2NO_2$ (brown gas)

Q46. PCl_5 is ionic in solid state.

Ans. PCl_5 is ionic in the solid state because it exists as $[PCl_4]^+[PCl_6]^-$ in which the cation is tetrahedral and anion is octahedral.

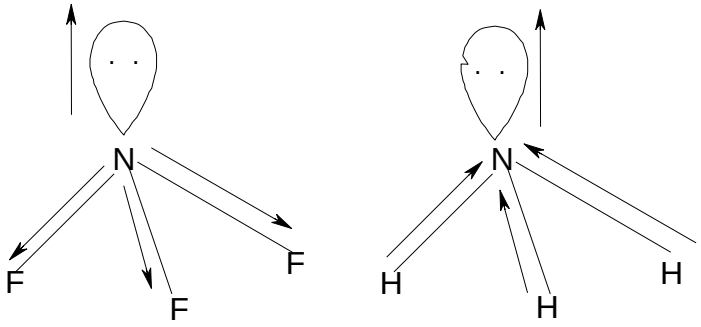
Q47. Concentrated HNO_3 turns yellow on exposure to sunlight. Why?

Ans. On exposure to sunlight, nitric acid decomposes into NO_2, O_2 and H_2O. The presence of NO_2 in the partially decomposed nitric acid, to gives it yellow colour.

$$4HNO_3\ (l) \rightarrow 4NO_2\ (g) + O_2\ (g) + 2H_2O\ (l)$$

Q48. NF_3 does not have donor properties like ammonia. Explain.

Ans. NF_3 has a pyramidal shape with one lone pair on N atom.



The lone pair on N is in opposite direction to the N – F bond moments and therefore, it has very low dipole moment (about 0.234 D). Thus, it does not show donor properties. But ammonia has high dipole moment because its lone pair is in same direction as the N – H bond moments. Thus, it has donor properties.

Q49. Ammonia is a good complexing agent. Explain.

Ans. Ammonia is a good complexing agent because of the presence of lone pair of electrons on nitrogen. This lone pair can easily be donated to electron deficient compounds forming complexes. For example, it reacts with Cu^{2+} ion to form a deep blue complex.

$$Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_2]^{2+}$$

Deep blue complex

Q50. Phosphoric acid has high viscosity and high melting point. Why?

Ans. Phosphoric acid has a tendency to form hydrogen bonding in concentrated solutions. Therefore, it has high viscosity and is a syrupy liquid and has high boiling point.

Q51. PCl_5 exists as $[PCl_4]^+[PCl_6]^-$ but PBr_5 exists as $[PBr_4]^+[Br]^-$. Explain.

Ans. Both PCl_5 and PBr_5 have trigonal bipyramidal geometry. This is not a regular structure and is not very stable. Therefore, PCl_5 splits up into more stable octahedral and tetrahedral structures, which are stable than trigonal bipyramidal. On the other hand, PBr_5 splits up into stable tetrahedral structure.

This splitting is different from PCl_5 because Br atoms are large and six atoms of Br cannot be easily accommodated around smaller P atom.

Q52. What is liquid nitrogen used for?

Ans. Liquid nitrogen is used as a refrigerant to preserve biological specimens. It is also used to provide low temperature.

Q53. Why does iron become passive when dipped in conc. HNO_3?

Ans. Iron becomes passive when dipped in conc. HNO_3 due to the formation of a thin protective layer of the metal oxide on its surface. This protective layer corresponds to ferrosoferric oxide, $FeO.Fe_2O_3$ and prevents further action of the metal.

Q54. What is calcium cyanamide? Why is it used as a fertilizer?

Ans. Calcium cyanamide is $CaCN_2$. It reacts with water to form ammonia.

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

So it can provide nitrogen nutrient to the soil and plants. Therefore, it is used as a fertilizer under name **nitrolim ($CaCN_2$ + C)**.

Q55. In the ring test of nitrates what chemical compound is formed?

Ans. $[Fe(H_2O)_5\ NO]SO_4$.

Q56. Give one reaction in which ammonia acts as a reducing agent.

Ans. When ammonia is passed over heated cupric oxide, copper is formed

$$3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$$

Q57. N_2O supports combustion more vigorously than air. Explain.

Ans. N_2O decomposes to give O_2 which is about 1/3 of the volume of gases produced ($2N_2 + O_2$). On the other hand, air contains 1/5 th part of O_2 of its volume. Due to larger content of O_2, N_2O supports combustion more vigorously than air.

Q58. Why is BiH_3 the strongest reducing agent amongst all the hydrides of group 15?

Ans. Among the hydrides of group 15, BiH_3 is least stable because Bi has largest size in the group and has least tendency
form covalent bond with small hydrogen atom. Therefore, it can readily lost H atom and has strongest tendency to act as to reducing agent.

Q59. Mention the conditions required to maximize the yield of ammonia.

Ans. Ammonia is formed according to the reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H^0 = -46.1\ kJ\ mol^{-1}$$

The conditions for maximum yield of ammonia are:

(i) Low temperature of the order of about 700 K.

(ii) High pressure of 200×10^5 Pa

(iii) Presence of catalyst such as iron oxide with small amount of K_2O and Al_2O_3.

Q60. Bond angle in PH_4^+ is higher than that in PH_3. Why?

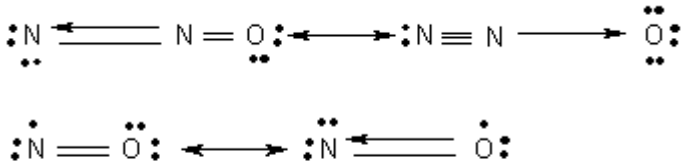
Ans. Both PH_4^+ and PH_3 involve sp^3 hybridisation of P atom. In PH^+_4 all the four orbitals are bonded, whereas in PH_3 there is a lone pair of electrons on P. PH_4^+, the H – P – H bond angle is tetrahedral angle of 109.5^0. But in PH_3,
lone pair - bond pair repulsion is more than bond pair – bond pair repulsion so that bond angles becomes less than normal tetrahedral angle of 109.5^0. The bond angle in PH_3 has been found to be about 93.6^0.

Q61. Write a balanced equation for the hydrolytic reaction of PCl_5 with heavy water.'
Ans. $PCl_5 + D_2O \rightarrow POCl_3 + 2DCl$

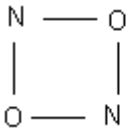
Q62. Draw the structure of all the oxides of nitrogen.
Ans.

Structure :-

Nitrogen has a tendency to form $P\pi - P\pi$ bonds. Therefore, the structures of its oxide are different to that of other oxide of group - 15 elements.

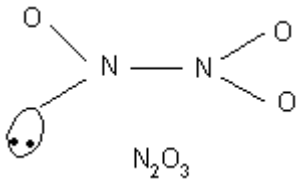


Paramagnetic

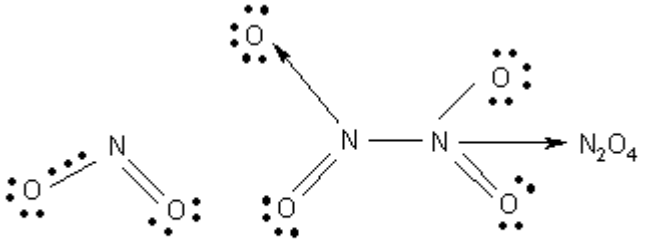


N_2O_2

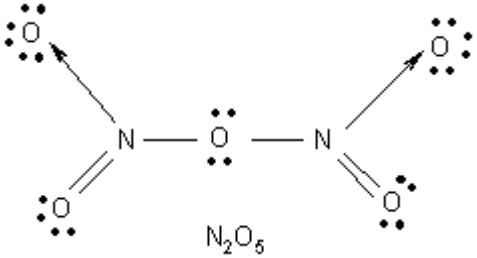
Diamagnetic



N_2O_3



NO_2



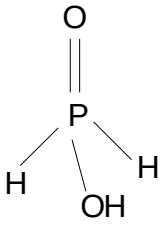
N_2O_5

Q63. Molecular nitrogen exist in the gaseous state while other member of group 15 exist in solid state. Why?
Ans. Physical state of molecules of group 15 elements can be explained on the basis of intermolecular forces of attraction. There are Vanderwaal's Intermolecular forces of attraction of molecules of group 15 elements. Vanderwaal's intermolecular forces of attraction are directly proportional to the molecular mass and surface area and both molecular mass and surface area increases down the group. Consequently, intermolecular forces of attraction increases down the group. That's why molecular nitrogen exsit in the gaseous state while other member of group 15 exist in solid state.
Q64. Give the structure of all the oxyacids of phosphorus. What are there basicity?
Ans. The structure are given below:-

H_3PO_2

Hypophosphorous acid

(Phosphinic acid)



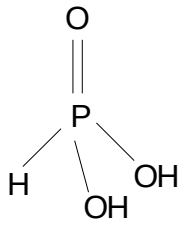
(P = +1)

Monobasic

H_3PO_3

Orthophosphorus acid

(Phosphonic acid)

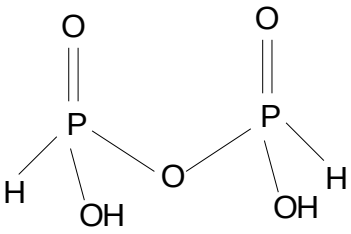


(P = +3)

Dibasic

$H_4P_2O_5$

Pyrophosphorus acid

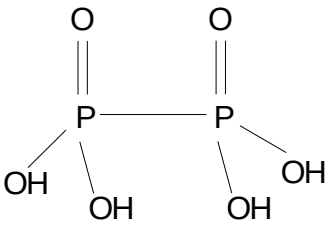


(P = +3)

Dibasic

$H_4P_2O_6$

Hypophosphoric acid

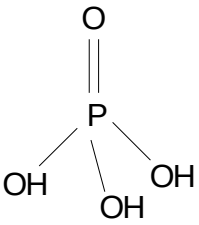


(P = +4)

Tetrabasic

H_3PO_4

Orthophosphoric acid

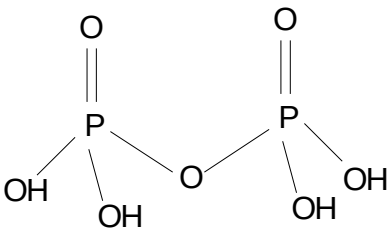


(P = +5)

Tribasic

$H_4P_2O_7$

Pyrophosphoric acid

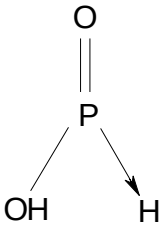


(P = +5)

Tetrabasic

HPO_3

Metaphosphoric acid

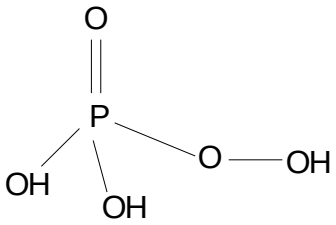


(P = +5)

Monobasic

H_3PO_5

Peroxomonophosphoric acid

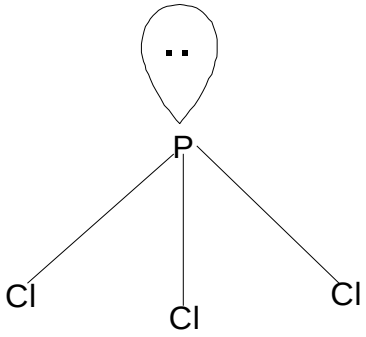


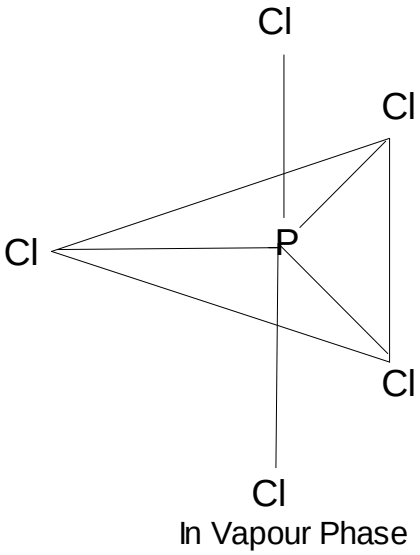
(P = +5)

Tribasic

Q65. Draw the structures of PCl_3 and PCl_5.

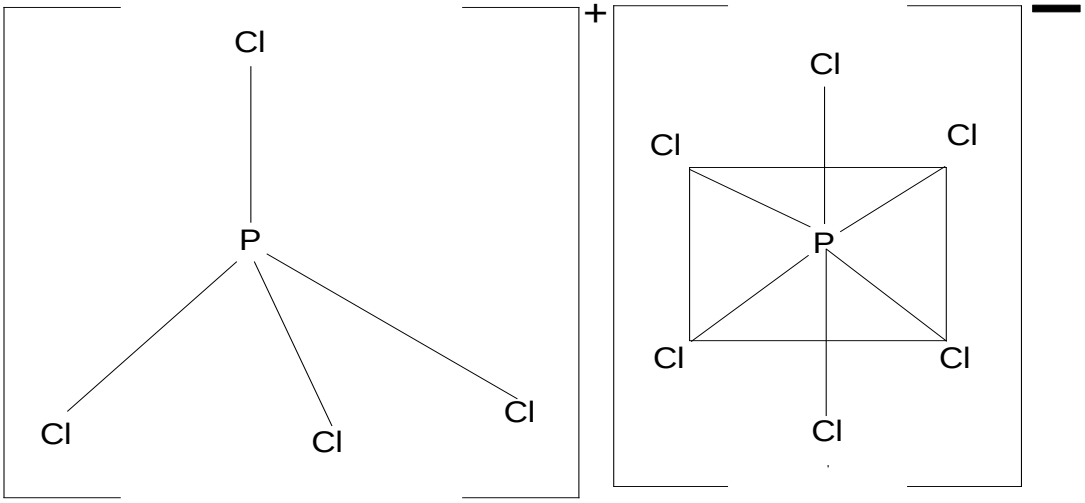
Ans. **<u>PCl_3 :-</u>** It has a pyramidal structure in which sp^3 hybridised phosphorus atom is attached with three chlorine atoms and fourth position is accupied by a lone pair.





In Vapour Phase

PCl$_5$:- X – ray studies confirm the ionic lattice of tetrahedral; $[PCl_4]^+$ $[PCl_6]^-$ in solid PCl_5. In vapour state, it consists of discrete PCl_5 molecules having trigonal bipyramidal shape.



PCl$_5$ in solid state

IMPORTANT REACTIONS OF GROUP – 15

1. Disproportionation reaction shows by the compound of Nitrogen

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

2. Laboratory prepatation of dinitrogen

$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 4H_2O(l) + NaCl(aq)$

3. Preparation of dinitrogen by the thermal decomposition of ammonium dichromate

$(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$

4. Preparation of very pure dinitrogen

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

5. $N_2 + O_2 \underset{}{\overset{Heat}{\rightleftharpoons}} 2NO$

6. Preparation of ammonia from urea

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

On a small scale ammonia is abtained from ammonium salts which decompose when treated with caustic soda or lime

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

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

On large scale, ammonia is manufactured by Haber's process

$$N_2(g) + 3H_2(g) \underset{700\ K,\ 200\ atm}{\overset{FeO(catalyst),\ K_2O\ \&\ Al_2O_3\ (Promoters)}{\rightleftharpoons}} 2NH_3(g)$$

7. $2FeCl_3(aq) + 3NH_4OH(aq) \rightarrow Fe_2O_3.xH_2O(s) + 3NH_4Cl(aq)$
8. $ZnSO_4(aq) + 2NH_4OH(aq) \rightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$
9. $Cu^{2+} + 4\ NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

(Blue) (Deep Blue)

10. $\underset{(White\ ppt.)}{Ag^+(s)} + 2NH_3(aq) \longrightarrow \underset{(Colourless)}{[Ag(NH_3)_2]^+(aq)}$

11. **Methods of preparation of oxides of Nitrogen**

Nitrous oxide (N_2O):

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

(molten)

$$H_2N_2O_2 \rightleftharpoons N_2O + H_2O$$

Nitric oxide (NO):

$$2NaNO_2 + FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$$

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

Dinitrogen trioxide (N_2O_3):

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

Nitrogen dioxide (NO_2):

$$2Pb(NO_3)_2 \underset{}{\overset{673\ K}{\rightleftharpoons}} 2PbO + 2NO_2 + O_2$$

Dinitrogen tetraoxide (N_2O_4):

$$2\,NO_2 \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} N_2O_4$$

Dinitrogen pentaoxide (N_2O_5):

$$2\,HNO_3 + P_2O_5 \longrightarrow 2\,HPO_3 + 2\,N_2O_5$$

12. Laboratory preparation of HNO_3
$NaNO_3 + H_2SO_4$ (conc.) $\rightarrow$ $NaHSO_4 + HNO_3$
On large scale HNO_3 is prepared mainly by Ostwald's process
$4NH_3\,(g) + 5O_2\,(g) \xrightarrow[500\,K,9\,bar]{Pt/Rh\ gauge\ catalyst} 4NO\,(g) + 6H_2O\,(g)$

$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$
$3NO_2\,(g) + H_2O\,(l) \rightarrow 2HNO_3\,(aq) + NO\,(g)$

13. Nitric acid act as a strong oxidizing agent

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

$$Cu + 4HNO_3(Conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$4Zn + 10HNO_3(dil.) \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$Zn + 4HNO_3(Conc.) \longrightarrow 4Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

some metals (e.g., Cr, Al) do not dissolve in conc. nitric acid because of the formation of a passive film of oxide on the surface.
Conc. nitric acid also oxidizes non – metals and their compounds. Iodine is oxidized to iodic acid, carbon to carbon dioxide, sulphur to H_2SO_4, and phosphorus to phosphoric acid.

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

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

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

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

14. **<u>Brown Ring Test:-</u>** The familiar brown ring test for nitrates depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex. The test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicate the presence of nitrate ion in solution.

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

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5(NO^+)]^{2+} + H_2O$$

15. $$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + \underset{(sodium\ hypophosphite)}{3NaH_2PO_2}$$

16. $$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

17. $$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

18. $$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$$

19. PH_3 When pure, it is non – inflammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

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

20. $$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

21. $$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$

22. Phosphine is weakly basic and like ammonia gives phosphonium compounds with acids

$$HBr + PH_3 \longrightarrow PH_4Br$$

23. $$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

24. $$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

25. $PCl_3 + 3H_2O \longrightarrow 3HCl + H_3PO_3$

26. $PCl_3 + 3CH_3COOH \longrightarrow 3CH_3COCl + H_3PO_3$

27. $PCl_3 + 3C_2H_5OH \longrightarrow 3C_2H_5Cl + H_3PO_3$

28. $P_4 + 10Cl_2 \longrightarrow 4PCl_5$

29. $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$

30. Reaction of PCl_5 with water

$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$

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

31. $PCl_5 \xrightarrow{Heat} PCl_3 + Cl_2$

32. $PCl_5 + CH_3COOH \longrightarrow POCl_3 + CH_3COCl + HCl$

33. It acts as an oxidizing agent

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

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

34. Orthophosphorous acid on heating disproportionates to give orthophosphoric acid and phosphine.

$4H_3PO_3 \xrightarrow{Heat} 3H_3PO_4 + PH_3$

35. The acids which contain P – H bond have strong reducing properties. Thus, hypophosphorous acid is a good reducing agent as it contains two P – H bonds and reduces.

$H_3PO_3 + 4AgNO_3 + 2H_2O \longrightarrow H_3PO_4 + 4HNO_3 + 4Ag$