7 THE P-BLOCK ELEMENTS

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. On addition of conc. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodide salt, violet fumes come out. This is because
   (*i*) H_2SO_4 reduces HI to I_2 (*ii*) HI is of violet colour
   (*iii*) HI gets oxidised to I_2 (*iv*) HI changes to HIO_3

Ans. (*iii*)

Explanation: When iodide salt reacts with H_2SO_4, HI is formed which is a strong reducing agent. It reduces H_2SO_4 to SO_2 and itself get oxidised to I_2.

$$H_2SO_4 + 2HI \rightarrow SO_2 + \underset{\text{(Violet colour)}}{I_2} + 2H_2O$$

2. In qualitative analysis when H_2S is passed through an aqueous solution of salt acidified with dil. HCl, a black precipitate is obtained. On boiling the precipitate with dil. HNO_3, it forms a solution of blue colour. Addition of excess of aqueous solution of ammonia to this solution gives _____.
   (*i*) deep blue precipitate of $Cu(OH)_2$
   (*ii*) deep blue solution of $[Cu(NH_3)_4]^{2+}$
   (*iii*) deep blue solution of $Cu(NO_3)_2$
   (*iv*) deep blue solution of $Cu(OH)_2.Cu(NO_3)_2$

Ans. (*ii*)

Explanation: When H_2S is passed through acidified solution of salt with dil. HCl black ppt is formed.

$$CuSO_4 + H_2S \xrightarrow{\text{dil HCl}} \underset{\text{Black ppt}}{CuS\downarrow} + H_2SO_4$$

On boiling CuS with dil. HNO_3 it forms blue coloured solution and the following reaction occur

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

$$S + 2HNO_3 \rightarrow H_2SO_4 + NO$$

$$2Cu^{2+} + SO_4^{2-} + 2NH_3 + 2H_2O \rightarrow Cu(OH)_2 . CuSO_4 + 2NH_4OH$$

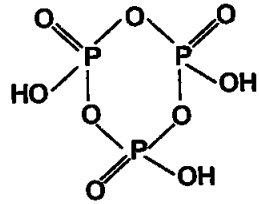
$$Cu(OH)_2 . CuSO_4 + 8NH_3 \rightarrow \underset{\substack{\text{Tetramine copper (II)}\\ \text{Deep blue solution}}}{2[Cu(NH_3)_4]SO_4} + 2OH^- + SO_4^{2-}$$

3. In a cyclotrimetaphosphoric acid molecule, how many single and double bonds are present?
   (*i*) 3 double bonds; 9 single bonds
   (*ii*) 6 double bonds; 6 single bonds

(*iii*) 3 double bonds; 12 single bonds
(*iv*) Zero double bonds; 12 single bonds

Ans. (*i*)

Explanation: Structure of Cyclotrimetaphosphoric acid



(Cyclotrimetaphosphoric acid)
3-double bonds, 9-single bonds

4. Which of the following elements can be involved in $p\pi$–$d\pi$ bonding?
(*i*) Carbon (*ii*) Nitrogen
(*iii*) Phosphorus (*iv*) Boron

Ans. (*iii*)

Explanation: Among four choices only phosphorous has vacant *d*-orbital

5. Which of the following pairs of ions are isoelectronic and isostructural?
(*i*) CO_3^{2-}, NO_3^- (*ii*) ClO_3^-, CO_3^{2-}
(*iii*) SO_3^{2-}, NO_3^- (*iv*) ClO_3^-, SO_3^{2-}

Ans. (*i*)

Explanation: No. of electron in both the molecule is = 32
Both has similar structure that is triangular planar.

6. Affinity for hydrogen decreases in the group from fluorine to iodine. Which of the halogen acids should have highest bond dissociation enthalpy?
(*i*) HF (*ii*) HCl
(*iii*) HBr (*iv*) HI

Ans. (*i*)

Explanation: On moving down the group atomic radii increases and bond dissociation enthalpy increases. So the highest bond dissociation enthalpy is of HF.

7. Bond dissociation enthalpy of E—H (E = element) bonds is given below. Which of the compounds will act as strongest reducing agent?

Compound	NH_3	PH_3	AsH_3	SbH_3
Δ_{diss} (E—H)/kJ mol–1	389	322	297	255

(*i*) NH_3 (*ii*) PH_3
(*iii*) AsH_3 (*iv*) SbH_3

Ans. (*iv*)

Explanation: On moving down the group size of the central atom increases *i.e.* bond length increases and bond dissociation enthalpy decreases.

8. On heating with concentrated NaOH solution in an inert atmosphere of CO_2, white phosphorus gives a gas. Which of the following statement is **incorrect** about the gas?

(*i*) It is highly poisonous and has smell like rotten fish.
(*ii*) It's solution in water decomposes in the presence of light.
(*iii*) It is more basic than NH_3.
(*iv*) It is less basic than NH_3.

Ans. (*iii*)

White phosphorous 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.

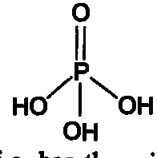
$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

9. Which of the following acids forms three series of salts?

(*i*) H_3PO_2 (*ii*) H_3BO_3
(*iii*) H_3PO_4 (*iv*) H_3PO_3

Ans. (*iii*)

Explanation: Structure of



H_3PO_4 has 3-OH groups i.e. has three ionisable H-atoms and hence forms three series of salts i.e., NaH_2PO_4, Na_2HPO_4, and Na_3PO_4.

10. Strong reducing behaviour of H_3PO_2 is due to

(*i*) Low oxidation state of phosphorus
(*ii*) Presence of two–OH groups and one P–H bond
(*iii*) Presence of one–OH group and two P–H bonds
(*iv*) High electron gain enthalpy of phosphorus

Ans. (*iii*)

Explanation: In H_3PO_2, two H atoms are bonded directly to P atom which imparts reducing character to the acid.

11. On heating lead nitrate forms oxides of nitrogen and lead. The oxides formed are _____.

(*i*) N_2O, PbO (*ii*) NO_2, PbO
(*iii*) NO, PbO (*iv*) NO, PbO_2

Ans. (*ii*)

Explanation: $2PbNO_3 \rightarrow 2PbO + 4NO_2 + O_2$

12. Which of the following elements does not show allotropy?

(*i*) Nitrogen (*ii*) Bismuth
(*iii*) Antimony (*iv*) Arsenic

Ans. (*i*)

Explanation: The single N—N bond is weak because of high inter-electronic repulsion of the non-bonding electrons, owing to the

small bond length. As a result the catenation tendency is weaker in nitrogen that is why it does not show allotropy.

13. Maximum covalency of nitrogen is _____.

(*i*) 3 (*ii*) 5

(*iii*) 4 (*iv*) 6

Ans. (*iii*)

Explanation: The electronic configuration of nitrogen is ns^2np^3. Nitrogen is restricted to the maximum covalency of 4 since only four (one *s* and three *p*) orbitals are available for bonding.

14. Which of the following statements is wrong?

(*i*) Single N–N bond is stronger than the single P–P bond.

(*ii*) PH_3 can act as a ligand in the formation of coordination compound with transition elements.

(*iii*) NO_2 is paramagnetic in nature.

(*iv*) Covalency of nitrogen in N_2O_5 is four.

Ans. (*i*)

Explanation: N—N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length.

15. A brown ring is formed in the ring test for NO_3^- ion. It is due to the formation of

(*i*) $[Fe(H_2O)_5(NO)]^{2+}$ (*ii*) $FeSO_4.NO_2$

(*iii*) $[Fe(H_2O)_4(NO)_2]^{2+}$ (*iv*) $FeSO_4.HNO_3$

Ans. (*i*)

Explanation: When freshly prepared solution of $FeSO_4$ is added in a solution containing NO_3^- ion, it leads to the formation of brown coloured complex.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow O + 3Fe^{2+} + 2H_2O$$

$$[Fe(H_2O)6]^{2+} + NO \rightarrow \underset{\text{Brownish}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

16. Elements of group-15 form compounds in +5 oxidation state. However, bismuth forms only one well characterised compound in +5 oxidation state. The compound is

(*i*) Bi_2O_5 (*ii*) BiF_5

(*iii*) $BiCl_5$ (*iv*) Bi_2S_5

Ans. (*ii*)

Explanation: Stability of +5 state decreases from top to bottom but because of high electronegativity and smaller size of fluorine bismuth can exist in this form.

17. On heating ammonium dichromate and barium azide separately we get

(*i*) N_2 in both cases

(*ii*) N_2 with ammonium dichromate and NO with barium azide

(*iii*) N_2O with ammonium dichromate and N_2 with barium azide
(*iv*) N_2O with ammonium dichromate and NO_2 with barium azide

Ans. (*i*)

Explanation: On heating ammonium dichromate and barium azide separately we get N_2 gas in both cases.

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

$Ba(N_3)_2 \rightarrow Ba + 3N_2$

18. In the preparation of HNO_3, we get NO gas by catalytic oxidation of ammonia. The moles of NO produced by the oxidation of two moles of NH_3 will be _____.

(*i*) 2 (*ii*) 3
(*iii*) 4 (*iv*) 6

Ans. (*i*)

Explanation: $4NH_3 + 5O_2 \xrightarrow[Pt]{\Delta} 4NO(g) + 6H_2O$

Hence, from above equation, oxidation of 2 moles of ammonia will produce 2 moles of NO.

19. The oxidation state of central atom in the anion of compound NaH_2PO_2 will be _____.

(*i*) +3 (*ii*) +5
(*iii*) +1 (*iv*) –3

Ans. (*iii*)

Explanation: Oxidation state of NaH_2PO_2

$\overset{+1}{Na}\ \overset{+1}{H_2}\ \overset{x}{P}\ \overset{-2}{O_2}$

$+1 + 2\times + 1 + x + 2 \times -2 = 0$

$+3 + x - 4 = 0$

$x - 1 = 0$

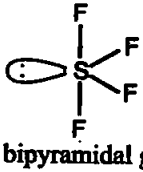
$x = +1$

20. Which of the following is not tetrahedral in shape?

(*i*) NH_4^+ (*ii*) $SiCl_4$
(*iii*) SF_4 (*iv*) SO_4^{2-}

Ans. (*iii*)

Explanation:



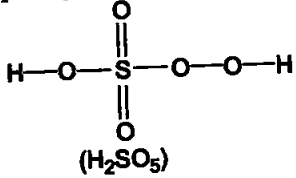
It has trigonal bipyramidal geometry having sp^3d hybridisation.

21. Which of the following are peroxoacids of sulphur?

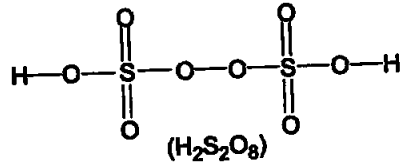
(*i*) H_2SO_5 and $H_2S_2O_8$ (*ii*) H_2SO_5 and $H_2S_2O_7$
(*iii*) $H_2S_2O_7$ and $H_2S_2O_8$ (*iv*) $H_2S_2O_6$ and $H_2S_2O_7$

Ans. (*i*)

Explanation: Peroxoacids of sulphur must contain —O—O— or peroxy linkage.



(H_2SO_5)



$(H_2S_2O_8)$

22. Hot conc. H_2SO_4 acts as moderately strong oxidising agent. It oxidises both metals and nonmetals. Which of the following element is oxidised by conc. H_2SO_4 into two gaseous products?

(*i*) Cu (*ii*) S

(*iii*) C (*iv*) Zn

Ans. (*iii*)

Explanation: Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2. C is oxidised into two gaseous products.

$$C + 2H_2SO_4(conc.) \rightarrow CO_2 + 2SO_2 + 2H_2O$$

23. A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH_3 an unstable trihalide is formed. In this process the oxidation state of nitrogen changes from _____.

(*i*) -3 to $+3$ (*ii*) -3 to 0

(*iii*) -3 to $+5$ (*iv*) 0 to -3

Ans. (*i*)

Explanation:

$$\underset{\text{(Black)}}{MnO_2} + 4HCl \rightarrow MnCl_2 + 2H_2O + \underset{\substack{\text{greenish}\\ \text{yellow gas}}}{Cl_2}$$

$$\overset{-3}{N}H_3 + 3Cl_2 \rightarrow \overset{+3}{N}Cl_3 + 3HCl$$

Hence oxidation state of nitrogen changes from -3 to $+3$.

24. In the preparation of compounds of Xe, Bartlett had taken $O_2^+ Pt F_6^-$ as a base compound. This is because

(*i*) both O_2 and Xe have same size.

(*ii*) both O_2 and Xe have same electron gain enthalpy.

(*iii*) both O_2 and Xe have almost same ionisation enthalpy.

(*iv*) both Xe and O_2 are gases.

Ans. (*iii*)

Explanation: Neil Bartlett, then observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+ Pt F_6^-$.

He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol^{-1}) was almost identical with that of xenon (1170 kJ mol^{-1}).

25. In solid state PCl_5 is a _____.

(*i*) covalent solid

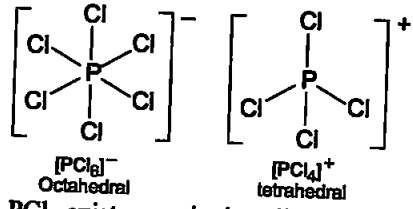
(*ii*) octahedral structure

(*iii*) ionic solid with $[PCl_6]$+ octahedral and $[PCl_4]$– tetrahedra

(*iv*) ionic solid with $[PCl_4]$+ tetrahedral and $[PCl_6]$– octahedra

Ans. (*iv*)

Explanation:



$[PCl_6]^-$ Octahedral $\quad$ $[PCl_4]^+$ tetrahedral

In solid state PCl_5 exist as an ionic solid with $[PCl_4]^+$ tetrahedral and $[PCl_6]^-$ octahedral.

26. Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power.

Ion	ClO_4^-	IO_4^-	BrO_4^-
Reduction potential $E^\ominus$/V	$E^\ominus$=1.19V	$E^\ominus$=1.65V	$E^\ominus$=1.74V

(*i*) $ClO_4^- > IO_4^- > BrO_4^-$ $\quad$ (*ii*) $IO_4^- > BrO_4^- > ClO_4^-$

(*iii*) $BrO_4^- > IO_4^- > ClO_4^-$ $\quad$ (*iv*) $BrO_4^- > ClO_4^- > IO_4^-$

Ans. (*iii*)

Explanation: Higher the standard reduction potential higher will be the oxidizing power.

27. Which of the following is isoelectronic pair?

(*i*) ICl_2, ClO_2 $\quad$ (*ii*) BrO_2^-, BrF_2^+

(*iii*) ClO_2, BrF $\quad$ (*iv*) CN^-, O_3

Ans. (*ii*)

Explanation: Isoelectronic species means no. of electron is same.

BrO_2^- (no. of electron) = 35 + 16 + 1 = 52

BrF_2^+ (no. of electron) = 35 + 17 = 52

II. Multiple Choice Questions (Type-II)

Note : In the following questions two or more options may be correct.

28. If chlorine gas is passed through hot NaOH solution, two changes are observed in the oxidation number of chlorine during the reaction. These are _____and _____.

(*i*) 0 to +5 $\quad$ (*ii*) 0 to +3

(*iii*) 0 to –1 $\quad$ (*iv*) 0 to +1

Ans. (*i*) and (*iii*)

Explanation: $6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

When chlorine gas is passed through hot NaOH solution it produces NaCl and $NaClO_3$. Thus oxidation state of chlorine changes from 0 to –1 and 0 to +5 respectively.

29. Which of the following options are not in accordance with the property mentioned against them?

(*i*) $F_2 > Cl_2 > Br_2 > I_2$	Oxidising power.
(*ii*) MI > MBr > MCl > MF	Ionic character of metal halide.
(*iii*) $F_2 > Cl_2 > Br_2 > I_2$	Bond dissociation enthalpy.
(*iv*) HI < HBr < HCl <HF	Hydrogen-halogen bond strength.

Ans. (*ii*) and (*iii*)

Explanation: MI < MBr <MCl < MF this is the correct order of ionic metal halide.

The correct order of bond dissociation enthalpy is $Cl_2 > Br_2 > F_2 > I_2$

Due to electronic repulsion among lone-pairs in F_2 molecule.

30. Which of the following is correct for P_4 molecule of white phosphorus?

(*i*) It has 6 lone pairs of electrons.

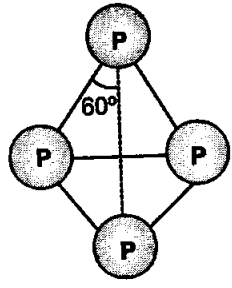
(*ii*) It has six P–P single bonds.

(*iii*) It has three P–P single bonds.

(*iv*) It has four lone pairs of electrons.

Ans. (*ii*) and (*iv*)

Explanation:



It has four lone pairs of electrons at each p-atom

It has six p-p single bond.

31. Which of the following statements are correct?

(*i*) Among halogens, radius ratio between iodine and fluorine is maximum.

(*ii*) Leaving F—F bond, all halogens have weaker X—X bond than X—X' bond in interhalogens.

(*iii*) Among interhalogen compounds maximum number of atoms are present in iodine fluoride.

(*iv*) Interhalogen compounds are more reactive than halogen compounds.

Ans. (*i*), (*iii*) and (*iv*)

Explanation: (*i*) Among group 17 elements radius ratio of iodine and fluorine is maximum because size of iodine is largest and fluorine is smallest in the group.

(*ii*) The correct statement is inter halogen compounds are more reactive than halogens (except fluorine). This is because X—X' bond in interhalogens is weaker than X—X bond in halogens except F—F.

(*iii*) As the ratio between radii of X and X' increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum.

(*iv*) Interhalogen compounds are more reactive than halogens (except fluorine). This is because X—X' bond in interhalogens is weaker than X—X' bond in halogens.

32. Which of the following statements are correct for SO_2 gas?

(*i*) It acts as bleaching agent in moist conditions.

(*ii*) It's molecule has linear geometry.

(*iii*) It's dilute solution is used as disinfectant.

(*iv*) It can be prepared by the reaction of dilute H_2SO_4 with metal sulphide.

Ans. (*i*) and (*iii*)

Explanation: SO_2 is used in bleaching of wool and silk and as an anti-chlor, disinfectant and preservative.

33. Which of the following statements are correct?

(*i*) All the three N—O bond lengths in HNO_3 are equal.

(*ii*) All P—Cl bond lengths in PCl_5 molecule in gaseous state are equal.

(*iii*) P_4 molecule in white phohsphorus have angular strain therefore white phosphorus is very reactive.

(*iv*) PCl is ionic in solid state in which cation is tetrahedral and anion is octahedral.

Ans. (*iii*) and (*iv*)

Explanation: (*i*) All the three N-O bond length in HNO_3 are not equal

(*ii*) In gaseous phase all P—Cl bond lengths in PCl_5 molecule are not equal.

(*iii*) White phosphorus is more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule.

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

34. Which of the following orders are correct as per the properties mentioned against each?

(*i*) $As_2O_3 < SiO_2 < P_2O_3 < SO_2$ Acid strength.

(*ii*) $AsH_3 < PH_3 < NH_3$ Enthalpy of vapourisation.

(*iii*) S < O < Cl < F More negative electron gain enthalpy.

(*iv*) $H_2O > H_2S > H_2Se > H_2Te$ Thermal stability.

Ans. (*i*) and (*iv*)

Explanation: (*i*) $As_2O_3 < SiO_2 < P_2O_3 < SO_2$

Order of acid strength

(*ii*) Correct order of enthalpy of vaporization is $AsH_3 > PH_3 > NH_3$

(*iii*) Correct order of more negative electron gain enthalpy $S < O < F < Cl$

(*iv*) Order of thermal stability —$H_2O > H_2S > H_2Se > H_2Te$

35. Which of the following statements are correct?

(*i*) S–S bond is present in $H_2S_2O_6$.

(*ii*) In peroxosulphuric acid (H_2SO_5) sulphur is in +6 oxidation state.

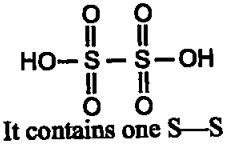
(*iii*) Iron powder along with Al_2O_3 and K_2O is used as a catalyst in the preparation of NH_3 by Haber's process.

(*iv*) Change in enthalpy is positive for the preparation of SO_3 by catalytic oxidation of SO_2.

Ans. (*i*) and (*ii*)

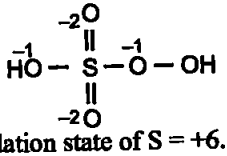
Explanation:

(*i*)



It contains one S—S bond.

(*ii*)



Oxidation state of S = +6.

(*iii*) Iron oxide with K_2O and Al_2O_3 is used to increase the rate of attainment of equilibrium in Haber's process.

(*iv*) Change in enthalpy is negative for the preparation of SO_3 by catalytic oxidation of SO_2.

36. In which of the following reactions conc. H_2SO_4 is used as an oxidising reagent?

(*i*) $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

(*ii*) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

(*iii*) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

(*iv*) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

Ans. (*ii*) and (*iii*)

Explanation: Among the above four (*ii*) and (*iii*) represent the oxidizing behaviour of H_2SO_4. In (*ii*) reaction it oxidizes HI and itself reduces to SO_2 oxidation state of central atom sulphur decreases from +6 to +4. In (*iii*) it oxidizes copper and itself get reduced to SO_2.

37. Which of the following statements are true?

(*i*) Only type of interactions between particles of noble gases are due to weak dispersion forces.

(*ii*) Ionisation enthalpy of molecular oxygen is very close to that of xenon.
(*iii*) Hydrolysis of XeF_6 is a redox reaction.
(*iv*) Xenon fluorides are not reactive.

Ans. (*i*) and (*ii*)

Explanation:

(*i*) Attraction in noble gases is due to weak dispersion force.
(*ii*) Ionisation enthalpy of molecular oxygen is very close to that of xenon.
(*iii*) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$ hydrolysis of XeF_6 is not a redox reaction.
(*iv*) Xenon fluorides are reactive in nature.

III. Short Answer Type

38. In the preparation of H_2SO_4 by Contact Process, why is SO_3 not absorbed directly in water to form H_2SO_4?

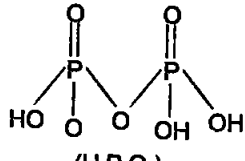
Ans. In contact process SO_3 is not absorbed directly in water to form H_2SO_4 because the reaction is highly exothermic and the reaction forms a corrosive aerosol that is very difficult to separate.

39. Write a balanced chemical equation for the reaction showing catalytic oxidation of NH_3 by atmospheric oxygen.

Ans. $4NH_3 + 5O_2 \xrightarrow[500\text{ k, }9\text{ bar}]{\text{Pt/Rh gauge catalyst}} 4NO + 6H_2O$

40. Write the structure of pyrophosphoric acid.

Ans. **Structure of pyrophosphoric acid:**



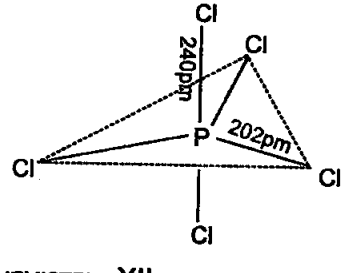
$(H_4P_2O_7)$

41. PH_3 forms bubbles when passed slowly in water but NH_3 dissolves. Explain why?

Ans. Because of H-bonding NH_3 dissolves in water whereas in PH_3 there is lack of H-bonding that is why it remains as gas and form bubbles in water.

42. In PCl_5, phosphorus is in sp^3d hybridised state but all its five bonds are not equivalent. Justify your answer with reason.

Ans. In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The 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.



43. Why is nitric oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic?

Ans. NO has 11 valence electrons. It is impossible for them all to be paired, and hence this is an odd number of valence electron and thus the gas is paramagnetic. It is diamagnetic in liquid and solid states, because the molecule dimerises to convert into stable N_2O_4 molecule with even numbers of electrons.

44. Give reason to explain why ClF_3 exists but FCl_3 does not exist.

Ans. Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX′, XX_3', XX_5' and XX_7' where X is a larger size halogen and X′ is a smaller size halogen. Fluorine is smallest in size due to high electronegativity therefore it cannot form FCl_3 whereas reverse is true.

45. Out of H_2O and H_2S, which one has higher bond angle and why?

Ans. As size of oxygen is small and due to its high electronegativity than sulphur O—H bond becomes more closer and bond pair-bond pair repulsion will be more. So, H_2O has higher bond angle than H_2S.

46. SF_6 is known but SCl_6 is not. Why?

Ans. Due to small size of fluorine, sulphur can accommodate 6 'F' atom around it. Chlorine is comparatively larger in size therefore because of interionic repulsion with chlorine SCl_6 is not known.

47. On reaction with C_{12}, phosphorus forms two types of halides 'A' and 'B'. Halide A is yellowish-white powder but halide 'B' is colourless oily liquid. Identify A and B and write the formulas of their hydrolysis products.

Ans. Halide 'A' is PCl_5 and 'B' is PCl_3 their hydrolysis reaction are as follows:

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

(A)

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

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

(B)

48. In the ring test of NO_3^- ion, Fe^{2+} ion reduces nitrate ion to nitric oxide, which combines with $Fe^{2+}(aq)$ ion to form brown complex. Write the reactions involved in the formation of brown ring.

Ans.

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

$$\underset{\text{(brown)}}{[Fe(H_2O)_6]^{2+}} + NO \rightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

49. Explain why the stability of oxoacids of chlorine increases in the order given below:

$$HClO < HClO_2 < HClO_3 < HClO_4$$

Ans. The more oxygen atom that are bonded with the oxoacids the electrons will be pulled away from the O—H bond, and the more this bond will

be weakend. Thus $HClO_4$ requires the least energy to break the O—H bond and form H^+. Hence $HClO_4$ is the strongest acid, and the order of stability is $HClO < HClO_2 < HClO_3 < HClO_4$.

50. Explain why ozone is thermodynamically less stable than oxygen.

Ans. Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen.

51. P_4O_6 reacts with water according to equation $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$. Calculate the volume of 0.1 M NaOH solution required to neutralise the acid formed by dissolving 1.1 g of P_4O_6 in H_2O.

Ans. $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$ ...(*i*)

For neutralisation

$4 \times H_3PO_3 + 2NaOH \rightarrow Na_2HPO_3 + 2H_2O$ ...(*ii*)

Adding eq. (*i*) and (*ii*)

$P_4O_6 + 8\ NaOH \rightarrow 4Na_2HPO_3 + 2H_2O$

P_4O_6 (mol. mass) = $(4 \times 31 + 16 \times 6) = 220$

Number of moles of

$$P_4O_6 = \frac{\text{Given mass}}{\text{Molar mass}} = \frac{1.1}{220}$$

$\because$ Product formed by $\frac{1.1}{220}$ of P_4O_6 will be neutralised by 8 moles of NaOH.

$\therefore$ Product formed by $\frac{1.1}{220}$ of P_4O_6 will be neutralised by NaOH.

$$P_4O_6 = 8 \times = \frac{1.1}{220} = \frac{8.8}{220} \text{ mol NaOH}$$

Given molarity of NaOH in 1L = 0.1 M

$$\text{Molarity} = \frac{\text{No. of moles}}{\text{Volume in litres}}$$

$$\text{Volume} = \frac{\text{No. of moles}}{\text{Molarity}}$$

$$= \frac{8.8}{220} \times \frac{1}{0.1} = 0.4\text{L}$$

52. White phosphorus reacts with chlorine and the product hydrolyses in the presence of water. Calculate the mass of HCl obtained by the hydrolysis of the product formed by the reaction of 62 g of white phosphorus with chlorine in the presence of water.

Ans. $P_4 + 6Cl_2 \rightarrow 4PCl_3$ ...(*i*)

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$ } × 4 ...(*ii*)

On adding eq. (*i*) and (*ii*)

$$P_4 + 6Cl_2 \rightarrow \cancel{4PCl_3}$$
$$\cancel{4PCl_3} + 12H_2O \rightarrow 4H_3PO_3 + 12HCl$$
$$P_4 + 6Cl_2 + 12H_2O \rightarrow 4H_3PO_3 + 12HCl$$

$31 \times 4 = 124$ g $\qquad 12 \times 36.5 = 438.0$ g

∵ 124 g white phosphorous produces 438g of HCl.

∴ 62 g white phosphorous will produce HCl.

$$\frac{438}{124} \times 62 = 219.0 \text{ g HCl}$$

53. Name three oxoacids of nitrogen. Write the disproportionation reaction of that oxoacid of nitrogen in which nitrogen is in +3 oxidation state.

Ans. Three oxoacids of nitrogen are:

(*i*) HNO_3 (Nitric acid)

(*ii*) HNO_2 (Nitrous acid)

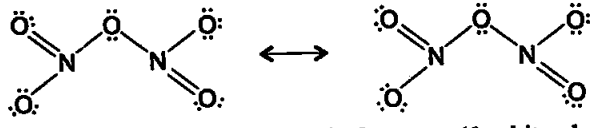
(*iii*) $H_2N_2O_2$ (Hyponitrous acid)

$$3HNO_2 \xrightarrow{\text{disproportionation}} HNO_3 + H_2O + 2NO$$

54. Nitric acid forms an oxide of nitrogen on reaction with P_4O_{10}. Write the reaction involved. Also write the resonating structures of the oxide of nitrogen formed.

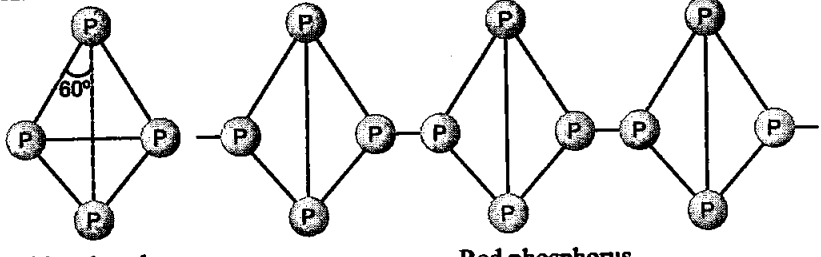
Ans. $4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$

Resonating structure of N_2O_5 are



55. Phosphorus has three allotropic forms — (*i*) white phosphorus (*ii*) red phosphorus and (*iii*) black phosphorus. Write the difference between white and red phosphorus on the basis of their structure and reactivity.

Ans.



White phosphorus Red phosphorus

White phosphorus is more reactive than red phosphorus because white P exists as discrete P_4 molecules. In red P several P_4 tetrahedra molecules are linked to formed polymeric chain.

Black phosphorus is the most stable form of phosphorus it is least reactive among all the allotropic form of phosphorus.

56. Give an example to show the effect of concentration of nitric acid on the formation of oxidation product.

Ans. Nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

For an example

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

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

57. PCl_5 reacts with finely divided silver on heating and a white silver salt is obtained, which dissolves on adding excess aqueous NH_3 solution. Write the reactions involved to explain what happens.

Ans. Finely divided metals on heating with PCl_5 give corresponding chlorides.

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

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+Cl^-(aq)$$

58. Phosphorus forms a number of oxoacids. Out of these oxoacids phosphinic acid has strong reducing property. Write its structure and also write a reaction showing its reducing behaviour.

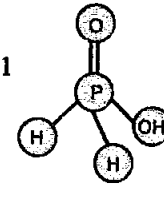
Ans. Hypophosphorus acid also known as phosphinic acid is a good reducing agent as it contains two P–H bonds and reduces, for example, $AgNO_3$ to metallic silver.

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

In the structure of phosphinic acid there is P = O = 1

P—OH = 1

P—H bond = 2



IV. Matching Type

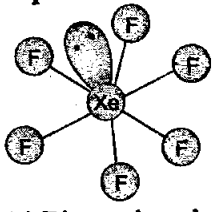
Note : Match the items of Column I and Column II in the following questions.

59. Match the compounds given in Column I with the hybridisation and shape given in Column II and mark the correct option.

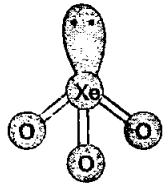
Column I	Column II
(A) XeF_6	(1) sp^3d^3 – distorted octahedral
(B) XeO_3	(2) sp^3d^2 – square planar
(C) $XeOF_4$	(3) sp^3 – pyramidal
(D) XeF_4	(4) sp^3d^2 – square pyramidal

Ans. (*i*)

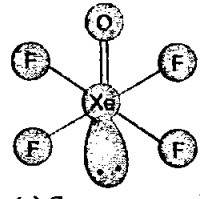
Explanation:



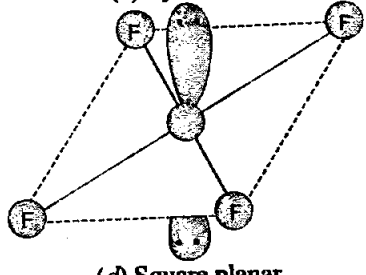
(*a*) Distorted octahedral



(*b*) Pyramidal



(*c*) Square pyramidal



(*d*) Square planar

60. Match the formulas of oxides given in Column I with the type of oxide given in Column II and mark the correct option.

Column I	Column II
(A) Pb_3O_4	(1) Neutral oxide
(B) N_2O	(2) Acidic oxide
(C) Mn_2O_7	(3) Basic oxide
(D) Bi_2O_3	(4) Mixed oxide

Code :

(*i*) A (1)	B (2)	C (3)	D (4)
(*ii*) A (4)	B (1)	C (2)	D (3)
(*iii*) A (3)	B (2)	C (4)	D (1)
(*iv*) A (4)	B (3)	C (1)	D (2)

Ans. (*ii*)

Explanation:

A. Pb_3O_4 is a mixed oxide.
B. N_2O is a neutral oxide.
C. Mn_2O_7 is a acidic oxide.
D. Bi_2O_3 is basic oxide.

61. Match the items of Columns I and II and mark the correct option.

Column I	Column II
(A) H_2SO_4	(1) Highest electron gain enthalpy
(B) CCl_3NO_2	(2) Chalcogen
(C) Cl_2	(3) Tear gas
(D) Sulphur	(4) Storage batteries

Code :

(*i*) A (4)	B (3)	C (1)	D (2)
(*ii*) A (3)	B (4)	C (1)	D (2)
(*iii*) A (4)	B (1)	C (2)	D (3)
(*iv*) A (2)	B (1)	C (3)	D (4)

Ans. (*i*)

Explanation:

A. H_2SO_4 is used in Storage batteries.

B. CCl_3NO_2 is known as tear gas.

C. Cl_2 has highest electron gain enthalpy.

D. Sulphur is also called as chalcogen.

62. Match the species given in Column I with the shape given in Column II and mark the correct option.

Column I	Column II
(A) SF_4	(1) Tetrahedral
(B) BrF_3	(2) Pyramidal
(C) BrO_3^-	(3) Sea-saw shaped
(D) NH_4^+	(4) Bent T-shaped

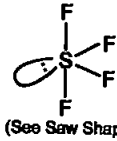
Code :

(*i*) A (3)	B (2)	C (1)	D (4)
(*ii*) A (3)	B (4)	C (2)	D (1)
(*iii*) A (1)	B (2)	C (3)	D (4)
(*iv*) A (1)	B (4)	C (3)	D (2)

Ans. (*ii*)

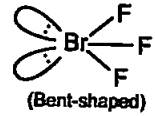
Explanation:

A. SF_4



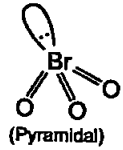
(See Saw Shaped)

B. BrF_3



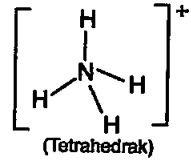
(Bent-shaped)

C. BrO_3^-



(Pyramidal)

D. NH_4^+



(Tetrahedrak)

63. Match the items of Columns I and II and mark the correct option.

Column I	Column II
(A) Its partial hydrolysis does not change oxidation state of central atom	(1) He
(B) It is used in modern diving apparatus	(2) XeF_6
(C) It is used to provide inert atmosphere for filling electrical bulbs	(3) XeF_4
(D) Its central atom is in sp^3d^2 hybridisation	(4) Ar

Code :

(*i*) A (1)	B (4)	C (2)	D (3)
(*ii*) A (1)	B (2)	C (3)	D (4)
(*iii*) A (2)	B (1)	C (4)	D (3)
(*iv*) A (1)	B (3)	C (2)	D (4)

Ans. (*iii*)

Explanation: A→Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$XeF_6 + H_2O \rightarrow XeOF_4 + 2\ HF$

$XeF_6 + 2\ H_2O \rightarrow XeO_2F_2 + 4HF$

We can see that oxidation state of central atom Xe remains unchanged.

B. He is used in modern diving apparatus

C. Ar is used to provide inert atmosphere for filling electrical bulbs

D. XeF_4 has Sp^3d^2 hybridization (4-bond pair and 2-lone pair)

V. Assertion and Reason Type

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*i*) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(*ii*) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(*iii*) Assertion is correct, but reason is wrong statement.

(*iv*) Assertion is wrong but reason is correct statement.

(*v*) Both assertion and reason are wrong statements

64. Assertion : N_2 is less reactive than P_4.
Reason : Nitrogen has more electron gain enthalpy than phosphorus.

Ans. (*iii*) Assertion is correct, but reason is wrong statement.

Explanation: N_2 is less reactive than P_4 molecule this is so, because nitrogen has very high bond dissociation enthalpy because of triple bond between two nitrogen atom which is not the case with phosphorus.

65. Assertion : HNO_3 makes iron passive.
Reason : HNO_3 forms a protective layer of ferric nitrate on the surface of iron.

Ans. (*iii*)

Explanation: HNO_3 makes iron passive . HNO_3 forms a protective layer of oxides on the surface of iron.

66. Assertion : HI cannot be prepared by the reaction of KI with concentrated H_2SO_4

Reason : HI has lowest H–X bond strength among halogen acids.

Ans. (*ii*)

Explanation: HI cannot be prepared by the reaction of KI with concentrated H_2SO_4 because HI formed is converted to I_2.

67. Assertion : Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2.

Reason : Oxygen forms $p\pi - p\pi$ multiple bond due to small size and small bond length but $p\pi - p\pi$ bonding is not possible in sulphur.

Ans. (*i*)

Explanation: Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2. Oxygen forms $p\pi - p\pi$ multiple bond due to small size and small bond length but $p\pi - p\pi$ bonding is not possible in sulphur due to its larger atomic size than oxygen.

68. Assertion : NaCl reacts with concentrated H_2SO_4 to give colourless fumes with pungent smell. But on adding MnO_2 the fumes become greenish yellow.

Reason : MnO_2 oxidises HCl to chlorine gas which is greenish yellow.

Ans. (*i*)

Explanation: NaCl reacts with concentrated H_2SO_4 to give colourless fumes with pungent smell. But on adding MnO_2 the fumes become greenish yellow. MnO_2 oxidises HCl to chlorine gas which is greenish yellow .

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ (fumes of HCl is colourless)

By heating manganese dioxide with concentrated hydrochloric acid.

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

69. Assertion : SF_6 cannot be hydrolysed but SF_4 can be.

Reason : Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6.

Ans. (*i*)

Explanation: SF_6 do not hydrolysed as it is in its maximum valency of six and it is insoluble in water. SF_4 can be hydrolyse as follows:

$SF_4 + 2H_2O \rightarrow SO_2 + 4HF$

VI. Long Answer Type

70. An amorphous solid "A" burns in air to form a gas "B" which turns lime water milky. The gas is also produced as a by-product during roasting of sulphide ore. This gas decolourises acidified aqueous $KMnO_4$ solution and reduces Fe^{3+} to Fe^{2+}. Identify the solid "A" and the gas "B" and write the reactions involved.

Ans. An amorphous solid 'A' is S_8 it react with air to form B (SO_2 (g)) which is a by-product of roasting of sulphide ore.

$$S_8 + 8O_2 \xrightarrow[\text{Heat}]{} 8SO_2$$

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2Fe^{2+}$$

71. On heating lead (II) nitrate gives a brown gas "A". The gas "A" on cooling changes to colourless solid "B". Solid "B" on heating with NO changes to a blue solid 'C'. Identify 'A', 'B' and 'C' and also write reactions involved and draw the structures of 'B' and 'C'.

Ans. Lead nitrate on heating produces brown gas 'A'

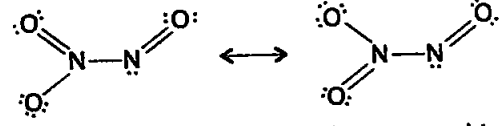
$$Pb(NO_3)_2 \xrightarrow[673k]{\Delta} \underset{\text{(Brown colour)}}{\overset{\text{A}}{2PbO + 4NO_2}}$$

Brown gas NO_2 is unstable on cooling it dimerises to colourless solid N_2O_4

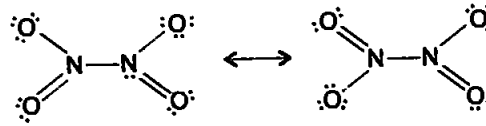
$$2NO_2 \underset{\Delta}{\overset{\text{On cooling}}{\rightleftharpoons}} \underset{\text{(Colourless solid)}}{\overset{\text{B}}{N_2O_4}}$$

$$2NO + N_2O_4 \rightarrow \underset{\text{(Blue solid)}}{\overset{\text{C}}{2N_2O_3}}$$

Structure of N_2O_3



Structure of N_2O_4



72. On heating compound (A) gives a gas (B) which is a constituent of air. This gas when treated with 3 mol of hydrogen (H_2) in the presence of a catalyst gives another gas (C) which is basic in nature. Gas C on further oxidation in moist condition gives a compound (D) which is a part of acid rain. Identify compounds (A) to (D) and also give necessary equations of all the steps involved.

Ans. $\underset{\text{'A'}}{NH_4NO_2} \rightarrow \underset{\text{'B'}}{N_2} + 2H_2O$

N_2 with 3 moles of H_2 in presence of catalyst form NH_3 gas which is basic in nature.

$$N_2 + 3H_2 \rightarrow \underset{\text{(C)}}{2NH_3}$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$4NO + O_2 \rightarrow 2NO_2$$

$$3NO_2 + H_2O \rightarrow \underset{\text{(D)}}{2HNO_3} + NO$$

□□□