THE p-BLOCK ELEMENTS

SOLVED SUBJECTIVE EXERCISE

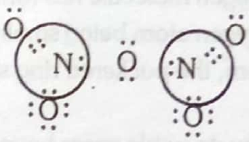
Very Short Answer Type Questions (1 mark)

1. Why are pentahalides more covalent than trihalides?

Ans. Higher the positive oxidation state of central atom, more will be its polarising power which, in turn, increases the covalent character of bond formed between the central atom and the other atom.
As, in petahalides, the central atom is in +5 oxidation state while in trihalides it is in +3 oxidation state. Therefore, pentahalides are more covalent than trihalides.

2. What is the covalence of nitrogen in N_2O_5?

Ans. Covalency depends upon the number of shared pair of electrons.
Now in N_2O_5, each nitrogen atom has four shared pairs of electrons as shown below :



Therefore, the covalency of N in N_2O_5 is 4.

3. How is O_3 estimated quantitatively?

Ans. When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating ozone gas.

4. Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water?

Ans. H_2SO_4 is a strong acid and gives H^+ ions readily in water. Therefore, K_{a_1} is very high.

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

But HSO_4^- is more resonance stabilised and gives second H^+ ion with difficulty. Hence $K_{a_2} << K_{a_1}$.

5. Why is ICl more reactive than I_2?

Ans. ICl is more reactive than I_2 because I—Cl bond is weaker than I–I bond. Consequently, ICl breaks easily to form halogen atoms which readily bring about the reactions.

6. Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group)?

Ans. N due to the absence of d-orbitals, cannot form $p\pi$–$d\pi$ multiple bonds. Thus, N cannot expand its covalency beyond four but in $R_3N = O$, N has a covalency of 5. So, the compound $R_3N = O$ does not exist. On the other hand, P due to the presence of d-orbitals forms $p\pi$–$d\pi$ multiple bonds and hence can expand its covalency beyond 4. Therefore, P forms $R_3P = O$ in which the covalency of P is 5.

7. Give the disproportionation reaction of H_3PO_3.

Ans. H_3PO_3 on heating disproportionates to give PH_3 in which P is reduced and H_3PO_4 in which P is oxidised.

$$4H_3\overset{+3}{P}O_3 \xrightarrow{\text{Heat}} \overset{-3}{P}H_3 + 3H_3\overset{+5}{P}O_4$$

Phosphorous acid → Phosphine + Orthophosphoric acid

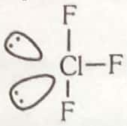
8. Can PCl_5 act as on oxidising as well as reducing agent? Justify.

Ans. The oxidation state of P in PCl_5 is +5. As P has five electrons in its valence shell, it cannot increase its oxidation state beyond +5 by donating electrons, therefore, PCl_5 cannot act as a reducing agent. However, it can decrease its oxidation number from +5 to +3 or some lower value, so, PCl_5 acts as an oxidising agent. For example, it oxidases Ag to AgCl, Sn to $SnCl_4$.

$$2\overset{0}{Ag} + \overset{+5}{P}Cl_5 \longrightarrow 2\overset{+1}{Ag}Cl + \overset{+3}{P}Cl_3; \quad \overset{0}{Sn} + 2\overset{+5}{P}Cl_5 \longrightarrow \overset{+4}{Sn}Cl_4 + 2\overset{+3}{P}Cl_3$$

9. Predict the shape of ClF_3 on the basis of VSEPR theory.

Ans. T-shape



10. Why does PCl_3 fume in moisture?

Ans. PCl_3 hydrolysis in the presence of moisture giving fumes of HCl.

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

11. Oxygen molecule has formula O_2 while sulphur S_8. Why?

Ans. Oxygen atom being small in size form multiple bond while S atom being large in size form single bond with other S atom, the puckered ring structure S_8 is most stable.

12. Why do noble gases have comparatively large atomic sizes?

Ans. The atomic size in the case of noble gases is expressed in terms of van der Waal's radii. Atomic size of other members of the period is either metallic radii or covalent radii. As the van der Waal's radii is larger than both metallic as well as covalent radii, the atomic size of the noble gas is quite large.

13. Can FCl_3 exist? Comment.

Ans. No, because F atom has no d-orbital and therefore it cannot expand its valance shell. Further, three big sized Cl atoms cannot be accommodated around a small F atom.

14. Why is the bond dissociation energy of fluorine molecule less than that of chlorine molecule?

Ans. Lower value of bond dissociation energy of F_2 is due to the strong repulsion between the non-bonding electrons of F atoms in the small sized F_2 molecule.

15. Write the balanced chemical equation for the reaction of Cl_2 with hot and concentrated NaOH. Is this reaction a disproportionation reaction? Justify.

Ans. $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

Yes, chlorine from zero oxidation state is changed to – 1 and + 5 oxidation states.

16. How does xenon atom form compounds with fluorine even though the xenon atom has a closed shell configuration?

Ans. This is because 1, 2 or 3 electrons from the 5 p-orbitals can be excited to empty 5d-orbitals thus making 2, 4 or 6 half-filled orbitals available for bond formation.

17. How would you account for the following :

NH_3 is a stronger base than PH_3.

Ans. This is because the lone pair of electrons on N atom in NH_3 is directed and not delocalised as it in PH_3 due to larger size of P.

18. Bleaching of flowers by chlorine is permanent while that by sulpur dioxide is temporary. Explain.

Ans. In presence of moisture, Cl_2 releases nascent oxygen which converts coloured material to colourless material. Thus, bleaching by Cl_2 is due to oxidation and hence permanent.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

Coloured material + [O] $\longrightarrow$ Colourless material

in contrast, in presence of moisture, SO_2 liberates nascent hydrogen which reduces coloured material to colourless material. Thus, bleaching with SO_2 is due to ***reduction***. When colourless material is exposed to air, it gets oxidised and the colour returns. Thus, bleaching by SO_2 is temporary.

19. Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group)?

Ans. N due to the absence of d-orbitals cannot form p? - d? multiple bonds. Thus, N cannot expand its covalency beyond four but in $R_3N = O$, N has a covalency of 5. So, the compound $R_3N = O$ does not exist. On the other hand. P due to the presence of d- orbitals forms $p\pi$ - $d\pi$ multiple bonds and hence can expand its covalency beyond 4. Therefore, P forms $R_3P = O$ in which the covalency of P is 5.

Short Answer Type Questions (2 mark)

20. How is the presence of SO_2 detected?

Ans. SO_2 is a pungent smelling gas. It can be detected by the following two tests:

(i) SO_2 turns acidified $K_2Cr_2O_7$ green due to reduction of $Cr_2O_7^{2-}$ to Cr^{3+} ions.

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-] \times 3$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$\underset{\text{(orange)}}{Cr_2O_7^{2-}} + 3SO_2 + 2H^+ \longrightarrow \underset{\text{(green)}}{2Cr^{3+}} + 3SO_4^{2-} + H_2O$$

(ii) SO_2 turns the pink violet colour of $KMnO_4$ colourless due to reduction of MnO_4 to Mn^{2+} ions

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-] \times 5$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$\underset{\text{(Pink voilet)}}{2MnO_4^-} + 5SO_2 + 2H_2O \longrightarrow \underset{\text{(Colourless)}}{2Mn^{2+}} + 5SO_4^{2-} + 4H^+$$

21. Why are halogens coloured?

Ans. All halogens are coloured. It is due to the reason that their molecules absorb light in the visible region as a result of which their electrons get excited to higher energy levels while the remaining light is transmitted. The colour of the halogens is actually the colour of this transmitted light. The amount of energy needed for excitation decreases progressively from F to I as the size of the atom increases. Hence, the energy of the transmitted light goes on increasing from F to I. In other words, the colour of the halogens deepens from F_2 to I_2. For example, F_2 absorbs violet light and hence appears pale yellow while iodine absorbs yellow and green light and hence appears deep violet. In the same way, we can account for greenish yellow colour of Cl_2 and orange red colour of bromine.

22. What inspired N Bartlett for carrying out reaction between Xe and PtF_6?

Ans. Neil Bartlett observed that PtF_6 reacts with O_2 to yield an ionic solid, $O_2^+ PtF_6^-$.

$$O_2(g) + PtF_6(g) \longrightarrow O_2^+[PtF_6]^-$$

Here, O_2 gets oxidised to O_2^+ by PtF_6.

Since the first ionization enthalpy of Xe (1170 kJ mol^{-1}) is fairly close to that of O_2 molecules (1175 kJ mol^{-1}), Bartlett thought that PtF_6 should also oxidise Xe to Xe^+. This inspired Bartlett to carry out the reaction between Xe and PtF_6. When Xe and PtF_6 were mixed, a rapid reaction took place and a red solid with the formula, $Xe^+ PtF_6^-$ was obtained.

$$Xe + PtF_6 \xrightarrow{278\ K} Xe^+[PtF_6]^-$$

23. Write balanced equations for the following :

(i) NaCl is heated with sulphuric acid in the presence of MnO_2.

(ii) Cl_2 gas is passed into a solution of NaI in water.

Ans. (i) Cl_2 is produced.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl] \times 4$$

$$4HCl + MnO_2 \longrightarrow MNCl_2 + Cl_2 + 2H_2O$$

$$4\,NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + Cl_2 + 2H_2O$$

(ii) Cl_2 being an oxidising agent oxidises NaI to I_2.

$$Cl_2(g) + 2NaI(aq) \longrightarrow 2NaCl(aq) + I_2(s)$$

24. Why is nitrous acid oxidant as well as reductant?

Ans. The oxidation state of N in nitrous acid (H—O—N = O) is +3 which lies in between its lowest oxidation state of –3 and highest oxidation state of +5. Since the oxidation state of N in (HNO_2) can be decreased from +3 to any lower value, therefore, it acts as an oxidising agent.

Further since the oxidation state of N in HNO_2 can be increased from +3 to +4 or +5, therefore, it acts as a reducing agent. Thus, nitrous acid acts both as an oxidant as well as a reductant.

25. Complete the following chemical reaction equations :

(i) $P_4(s) + NaOH(aq) + H_2O(l) \longrightarrow$

(ii) I^- (aq) + $H_2O(l) + O_3(g) \longrightarrow$

Ans. (i) $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2PO_2$

(ii) $2I^-(aq) + H_2O(l) + O_3(g) \longrightarrow 2\bar{O}H(aq) + I_2(s) + O_2(g)$

26. Complete the following chemical reaction equations:

(i) $XeF_2 + H_2O \longrightarrow$ (ii) $PH_3 + HgCl_2 \longrightarrow$

Ans. (i) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

(ii) $2PH_3 + \underset{\text{Mercuric Chloride}}{3HgCl_2} \longrightarrow \underset{\text{Mercuric phosphide}}{Hg_3P_2 \downarrow} + 6HCl$

27. Give reasons for the following observations:

(i) SF_6 is inert towards hydrolysis.

(ii) Sulphur exhibits greater tendency for catenation than selenium.

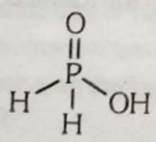
Ans. (i) In SF_6, S is sterically protected by six F atoms and hence does not allow H_2O molecules to attack the S atom. Further, F does not have d-orbitals to accept the electrons donated by H_2O molecules. As a result of these two reasons, SF_6 does not undergo hydrolysis. On the other hand, in SF_4, S is not sterically protected since it is surrounded by only four F atoms. Thus, attack of H_2O molecules can take place easily and hence hydrolysis occurs.

(ii) As we move from S to Se, the atomic size increases and hence the strength of E—E bond decreases. Thus, S—S bond is much stronger than Se—Se bond consequently, S shows greater tendency for catenation than selenium.

28. Write the structures of the following species :

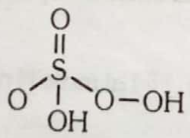
(i) H_3PO_2 (ii) H_2SO_5

Ans. (i)



Hypophosphorous acid

(ii)



Peroxomonosulphuric acid

29. Assign reasons for the following :

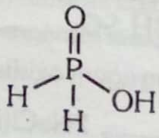
(i) The acid strengths of acids increase in the order

HF < HCl < HBr < HI

(ii) H_3PO_2 behaves as a monoprotic acid.

Ans. (i) This is due to decrease in the bond dissociation energy of H–X on moving top to bottom in a group.

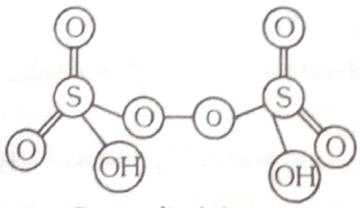
(ii) Since it contains only one ionizable H-atom which is present as OH group, therefore, it behave as a monoprotic acid.



30. Draw the structures of the following:

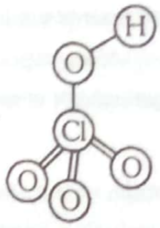
(i) $H_2S_2O_8$ (ii) $HClO_4$

Ans. (i)



Peroxodisulphuric acid
($H_2S_2O_8$)

(ii)



Perchloric acid
($HClO_4$)

Short Answer Type Questions (3 mark)

31. Arrange the following in order of property indicated for each set :

(i) F_2, Cl_2, Br_2, I_2–increasing bond dissociation enthalpy.

(ii) HF, HCl, HBr, HI–increasing acid strength.

(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_3–increasing base strength.

Ans. (i) Bond dissociation enthalpy decreases as the bond distance increases from F_2 to I_2 because of the corresponding increase in the size of the atom as we move from F to I. The F—F bond dissociation enthalpy is, however, smaller than that of Cl–Cl and even smaller than that of Br—Br. This is because F atom is very small and hence the three lone pairs of electrons on each F atom repel the bond pair holding the F-atoms in F_2 molecule. Hence, the bond dissociation enthalpy increases in the order; $I_2 < F_2 < Br_2 < Cl_2$.

(ii) As the size of atom increases from F to I the bond dissociation enthalpy of H—X bond decreases from H—F to H—I. Therefore, the acid strength increases in the opposite order.

HF < HCl < HBr < HI.

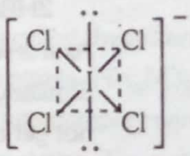
(iii) As we move from NH_3 to BiH_3, the size of the atom increases. Consequently, the electron density on the central atom decreases and hence the basic strength decreases as we move from NH_3 to BiH_3. Therefore, the basic strength increases in the order: $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$.

32. Give the formula and describe the structure of a noble gas species which is isostructural with :

(i) ICl_4^- (ii) IBr_2^- (iii) BrO_3^-.

Ans. ***(i) Structure of ICl_4^- :*** I in ICl_4^- has four bond pairs and two lone pairs. Therefore, according to VSEPR theory, it should be square planar as shown.

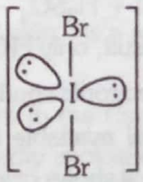
Here, ICl_4^- has $(7 + 4 \times 7 + 1) = 36$ valence electrons. A noble gas species having 36 valence electrons is XeF_4 $(8 + 4 \times 7 = 36)$. Therefore, like ICl_4^-, XeF_4 is also square planar.



Square Planar

(ii) Structure of IBr_2^- : I in IBr_2^- has two bond pairs and three lone pairs. So, according to VSEPR theory, it should be linear.

Here, IBr_2^- has $22(7 + 2 \times 7 + 1)$ valence electrons. A noble gas species having 22 valence electrons is XeF_2 $(8 + 2 \times 7 = 22)$. Thus, like IBr_2^-, XeF_2 is also linear.

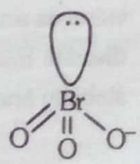


Linear

(iii) Structure of BrO_3^- : The central atom Br has seven electrons. Four of these electrons form two double bonds or coordinate bonds with two oxygen atoms while the fifth electron forms a single bond with O^- ion. The remaining two electrons form one lone pair. Hence, in all there are three bond pairs and one lone pair around Br atom in BrO_3^-. Therefore, according to VSEPR theory, BrO_3^- should be pyramidal.

Here, BrO_3^- has $26(7 + 3 \times 6 + 1 = 26)$ valence electrons.

A noble gas species having 26 valence electrons is XeO_3 $(8 + 3 \times 6 = 26)$. Thus, like BrO_3^-, XeO_3 is also pyramidal.



Pyramidal

33. Account for the following :

(a) Chlorine water has both oxidizing and bleaching properties.

(b) H_3PO_2 and H_3PO_3 act as good reducing agents while H_3PO_4 does not.

(c) On addition of ozone gas to KI solution, violet vapours are obtained.

Ans. (a) Chlorine water produces nascent oxygen which is responsible for bleaching action and oxidation.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

(b) Both H_3PO_2 and H_3PO_3 have P—H bonds, so they act as reducing agents, but H_3PO_4, has no P—H bond but has O—H bonds, so it cannot act as a reducing agent.

(c) Ozone gas acts as a strong oxidising agent, so it oxidises iodide ions to Iodine.

$$2I^{\ominus}(aq) + H_2O(l) + O_3(g) \longrightarrow 2OH^{\ominus}(aq) + I_2(g) + O_2(g)$$

I_2 vapours evolved have violet colour.

34. Give reasons:

(i) Xenon does not form fluorides such as XeF_3 and XeF_5.

(ii) Out of noble gases, only xenon is known to form established chemical compounds.

Ans. (i) All the filled orbitals of Xe have paired electrons. The promotion of one, two or three electrons from the 5p-filled orbitals to the 5d-vacant orbitals will give rise to two, four and six half-filled orbitals respectively. So Xe can combine with even but not odd number of F atoms. Hence, it cannot form XeF_3 and XeF_5.

(ii) Except radon which is radioactive, Xe has lowest ionization enthalpy among noble gases and hence it readily forms chemical compounds with strong oxidising agents such as O_2 and F_2.

35. Give reasons for the following:

(i) When NaBr is heated with conc. H_2SO_4, Br_2 is produced but when NaCl is heated with conc. HCl is produced.

(ii) Oxygen generally exhibits an oxidation state of –2 only whereas other members of its family show oxidation states of +2, +4 and +6 as well.

(iii) Among the hydrides of Group 16, water shows unusual physical properties.

Ans. (i) When NaBr is heated with conc. H_2SO_4, HBr is first produced which being a reducing agent reduces H_2SO_4 to SO_2 while HBr itself gets oxidised to Br_2.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$$

As a result, only Br_2 is produced.

Similarly, NaCl reacts with conc. H_2SO_4 to form HCl but since HCl does not act as a reducing agent, it does not get oxidised to Cl_2.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$HCl + H_2SO_4 \longrightarrow \text{No action}$$

As a result, only HCl is evolved.

(ii) The electronic configuration of oxygen is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$, i.e., it has two half-filled orbitals and there is no d-orbital available for excitation of electrons. Further, it is the most electronegative element of its family. Hence, it shows oxidation state of –2 only. Other elements like sulphur have d-orbitals available for excitation, thereby giving four and six half-filled orbitals. Moreover, they can combine with more electronegative elements. Hence, they show oxidation states of +2, +4 and +6 also.

(iii) Because of high electronegativity of O, the O—H in H_2O forms strong intermolecular H-bonds. Thus, water exists as an associated molecule while other hydrides of Group 16 do not form H-bonds and hence exist as discrete molecules. Hence, water shows unusual physical properties, i.e., high boiling point, high thermal stability and weaker acidic character as compared to other hydrides of Group 16.

EXERCISE-1

PREVIOUS YEARS BOARD PROBLEMS

CBSE 2016

1. On heating $Pb(NO_3)_2$ a brown gas is evolved which undergoes dimerization on cooling. Identify the gas.
2. Write the structures of the following :
   (i) $(HPO_3)_3$ (ii) XeF_4
3. Assign reason for the following :
   (i) H_3PO_2 is a stronger reducing agent than H_3PO_4.
   (ii) Sulphur shows more tendency for catenation than Oxygen.
   (iii) Reducing character increases for HF to HI.

CBSE 2015

1. Write the formulae of any two oxoacids of phosphorus.
2. (a) Account for the following
   (i) Bond angle in NH_4^+ is greater than that in NH_3.
   (ii) Reducing character decreases from SO_2 to TeO_2.
   (iii) $HClO_4$ is a stronger acid than HClO
   (b) Draw the structures of the following
   (i) $H_2S_2O_8$ (ii) $XeOF_4$
3. (a) Which poisonous gas is evolved when white phosphorus is heated with conc. NaOH solution ? Write the chemical equation.
   (b) Write the formula of first noble gas compound prepared by N. Bartlett. What inspired N. Bartlett to prepare this compound ?
   (c) Fluorine is a stronger oxidizing agent than chlorine. Why ?
   (d) Write one use of chlorine gas
   (e) Complete the following equation
   $CaF_2 + H_2SO_4 \rightarrow$

CBSE 2014

1. Complete the following equations :
   (i) $P_4 + H_2O \rightarrow$ (ii) $XeF_4 + O_2F_2 \rightarrow$
2. Draw the structures of the following :
   (i) XeF_2 (ii) BrF_3
3. Complete the following equations :
   (i) $C + conc.\ H_2SO_4 \rightarrow$ (ii) $XeF_2 + H_2O \rightarrow$
4. Draw the structures of the following :
   (i) XeO_3 (ii) H_2SO_4
5. Give reasons for the following :
   (i) $(CH_3)_3\ P = O$ exists but $(CH_3)_3\ N = O$ does not.
   (ii) Oxygen has less electron gain enthalpy with negative sign than sulphur.
   (iii) H_3PO_2 is a stronger reducing agent than H_3PO_3.

CBSE 2013

1. What is the covalency of nitrogen in N_2O_5?
2. What is the basicity of H_3PO_3 and why?
3. Give reasons for the following
   (i) Where R is an alkyl group, $R_3P = O$ exists but $R_3N = O$ does not.
   (ii) $PbCl_4$ is more covalent than $PbCl_2$.
   (iii) At room temperature, N_2 is much less reactive.

CBSE 2012

1. Draw the structure of the following molecule : H_3PO_2.
2. Explain the following
   The chemical reactivity of nitrogen is much less than that of phosphorus.
3. Which is a stronger reducing agent, SbH_3 or BiH_3 and why ?
4. NF_3 is an exothermic compound, whereas NCl_3 is not. Explain.
5. Draw the molecular structure of N_2O_5.
6. Complete the following equation
   $Cu + HNO_3(\text{dilute}) \longrightarrow$
7. What is the basicity of H_3PO_2 and why ?

CBSE 2011

1. What is the basicity of H_3PO_3 and why?
2. Draw the structure of $(HPO_3)_3$.
3. Complete the following chemical equation
   $HgCl_2 + PH_3 \longrightarrow$
4. The N—O bond in NO_2^- is shorter than the N—O bond in NO_3^-. Explain.
5. All the P—Cl bonds in PCl_5 molecule are not equivalent. Explain why ?
6. Nitrogen does not form pentahalides, although it exhibits +5 oxidation state. Explain.
7. Ammonia is more basic than phosphine. Why ?
8. Account for the following PCl_5 can act as an oxidising agent but not as a reducing agent.
9. What happens when H_3PO_3 (orthophosphorus acid) is heated ?

CBSE 2010

1. Why is BiH_3 the strongest reducing agent amongst all the hydrides of group 15 elements ?
2. Nitrogen shows weaker tendency for catenation than phosphorus. Explain.
3. Complete the following chemical reaction equations:
   (i) $I_2 + \text{conc.}HNO_3 \rightarrow$ (ii) $HgCl_2 + PH_3 \rightarrow$
4. Draw the structure of $H_2S_2O_8$.

CBSE 2009

1. In the structure of HNO_3 molecule, the N—O bond (121 pm) is shorter than N—OH bond (140 pm).
2. Draw the structure of $PCl_5(s)$.
3. Ammonia has higher boiling point than phosphine. Explain why?
4. Bi (V) is a stronger oxidising agent than Sb (V). Explain.
5. The basic character of the hydrides of group 15 elements decreases with increasing atomic numbers. Why ?
6. Complete the following reactions : $NH_3 + NaOCl \rightarrow$

EXERCISE-1

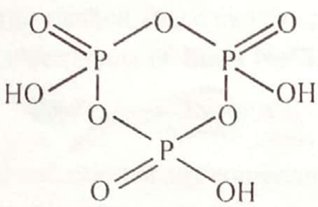
SOLUTION PREVIOUS YEARS BOARD PROBLEMS

THE P-BLOCK ELEMENT

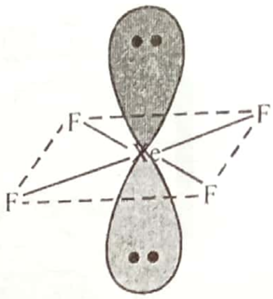
CBSE 2016

Sol.1 NO_2

Sol.2 (i)



(ii)



Sol.3 (i) Due to presence of two P-H bonds in H_3PO_2 / In H_3PO_2 O.S of P = +1 which can increase but in H_3PO_4 O.S of P =+5 (max.)

(ii) Due to stronger S-S bond than O-O bond.

(iii) Size of halogen increases / bond length increases /bond dissociation enthalpy decreases (any one)

CBSE 2015

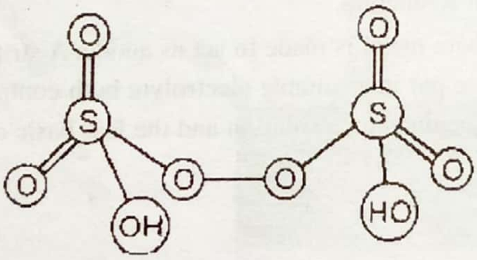
Sol.1 H_3PO_2, H_3PO_3, $H_4P_2O_5$, $H_4P_2O_6$, H_3PO_4, $H_4P_2O_7$, H_3PO_5, $H_4P_2O_8$, $(HPO_3)_3$, $(HPO_3)_n$ **(Any two)**

Sol.2 (a) (i) Due to lone pair of electron on nitrogen in NH_3

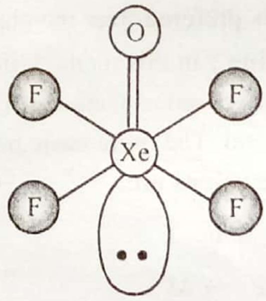
(ii) Due to inert pair effect / Stability of higher oxidation state decreases down the group from S to Te / Stability of lower oxidation state increases down the group

(iii) ClO_4^- is more stable than ClO– / ClO_4^- is weak conjugate base than ClO

(b) (i)



(ii)



Sol.3 (a) PH_3 $\quad P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

(b) $Xe + [PtF_6]^-$, Approximately same molecular size of Xe & O_2 / Comparable ionisation energies of Xe & O_2

(c) It is due to (i) low enthalpy of dissociation of F-F bond (ii) high hydration enthalpy of F^-.

(d) (i) for bleaching wood pulp (required for manufacture of paper and rayon), cotton and textiles.

(ii) In the metallurgy (extraction) of gold and platinum.

(iii) In the manufacture of dyes, drugs and organic compounds such as $CHCl_3$, CCl_4, DDT, refrigerants (CCl_2F_2, freon), and bleaching powder.

(iv) In the preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$), etc. Mustard gas was used by Germany in World War I.

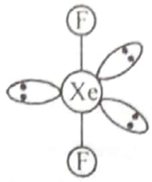
(v) In sterilizing drinking water. **(Any one use)**

(e) $CaF_2 + H_2SO_4\ CaSO_4 + 2HF$

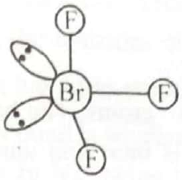
CBSE 2014

Sol.1 (i) $P_4 + 3H_2O + \xrightarrow{NaOH} PH_3 + 3NaH_2PO_2$

(ii) $XeF_4 + O_2F_2 \xrightarrow{143K} XeF_6 + O_2$

Sol.2 (i) XeF_2 :- 

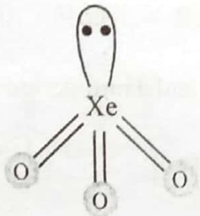
Linear

(ii) BrF_3 :- 

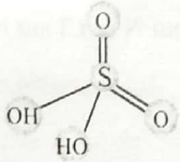
Bent 'T' shaped

Sol.3 (i) $C + 2H_2SO_4(conc.) \rightarrow CO_2 + 2SO_2 + 2H_2O$

(ii) $2XeF_2(s) + 2H_2O(l) \rightarrow 2Xe\ (g) + 4\ HF(aq) + O_2(g)$

Sol.4 (i) 

Pyramidal

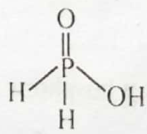
(ii) 

Sulphuric acid
(H_2SO_4)

Sol.5 (i) Nitrogen can not form dπ – pπ bond due to the absence of d-orbitals so, it cannot expand its covalency beyond four as the heavier members of this graeap an, eg $(CH_3)_3P = 0$ or $(CH_3)_3\ P = CH_2$.

(ii) The electron gain enthalpy for oxygen is less negative because of its small size due to which the electron repulsions in the relatively small 2P-subshell are comporatively carge and hence, the inceoming electrons are nof accepted with the same case as in case of sulphur as it has relatively large size.

(iii) Acids which contain large number of P–H bonds are good reducing agent

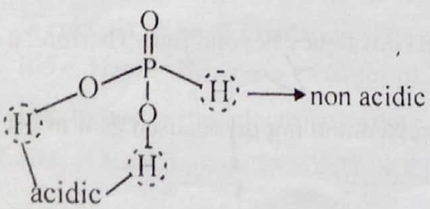


In H_3PO_2, there are two hydrogen atoms attached directly to P, i.e., it has two P–H bonds to which it shows reducing property.

CBSE 2013

Sol.1 Covalency depends upon the number of shared pairs of electrons. Since nitrogen atom has 4 shared electrons pairs, hence the covalency of nitrogen in N_2O_5 is 4.

Sol.2 The basicity of H_3PO_3 is 2 as there are two replacable / acidic Hydrogens and third H is directly attached to P hence not acidic in nature.

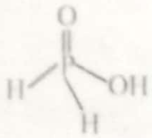


Sol.3 (i) Nitrogen can not form $d\pi - p\pi$ bond due to the absence of d-orbitals so, it cannot expand its covalency beyond four as the heavier members of this graeap an, eg $(CH_3)_3P = 0$ or $(CH_3)_3P = CH_2$.

(ii) Because of high oxidising power, halogens halides. But if the metal exhibits more than one oxidation states, the halide in the higher oxidation state will be more covalent than $PbCl_2$.

(iii) N_2 is less reactive at room temperature because of high bond enthalpy of a triple bond between N≡N.

CBSE 2012

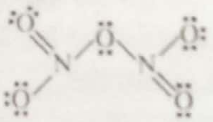
Sol.1 

Sol.2 Nitrogen exists as a diatomic molecule with a triple bond between two N – atoms. The bond dissociation enthalpy of this triplo bond (N≡N) is very high due to which nitrogen is inert and unreactive at room tomeratuse.

In contrast, phosphorus exists as a tetra atomic molecule (P_4). As P–P bond is much weaker than N≡N bond, therefore P–P bond can be broken easily and hence, phosphorus is much more reactive than nitrogen.

Sol.3 BiH_3, due to less bond dissociation enthalpy.

Sol.4 B'coz N & F are second period element (2p – 2p) but N & Cl are both second and Third period elements (2p – 3p).

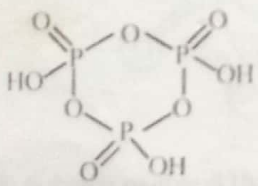
Sol.5 

Sol.6 $3Cu + 8HNO_3(dilute) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

Sol.7 Basicity of H_3PO_2 is one due to the presence of one replacable hydrogen atom.

CBSE 2011

Sol.1 Basicity of H_3PO_2 is one due to the presence of one replacable hydrogen atom.

Sol.2 

Cyclotrimeta p hosphoric acid $(HPO_3)_3$

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

Sol.4 The N–O bond in NO_2^- is shorter than the N–O bond in NO_3^-. Explain

Sol.5 In PCl_5, P is sp3d- hybiridised and thus, possesses trigonal bipgramidal geometry. It has three equaforial P-Cl bonds and two axial P-Cl bond. Since, two axial P-Cl bonds are repelled by three bond pairs while three equatorial P-Cl bonds are repelled by two bond pairs. Therefore, axial bonds are longer than equatorial bonds. Thus, all the five bonds in PCl_5 are not equaivalent.

Sol.6 Nitrogen does not have d-orbitals in its valence shell to expand its covalency beyond four. Therfore, it does not form pentahalides.

Sol.7 This because the lone pair of electrons on N-atom in NH_3 is directed and not delocalised as it in pH_3 due to larger size of P.

Sol.8 The oxidation state of P in PCl_5 is +5. As P has five electrons in its valence shell, it can not increase its oxidation state beyond +5 by donating electrons., therefore PCl_5 cannot act as a reducing agent. However, it can decrease its oxidation number form +5 to +3 or some lower value, so PCl_5 acts as an oxidising agent.

Sol.9 $H_3PO_3 \xrightarrow{\Delta} H_3PO_4 + PH_3$

CBSE 2010

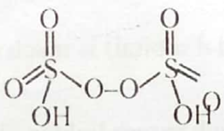
Sol.1 On moving down the group, the size of the element increases resuting in the increase in the length of E–H bond and hence, bond strength of E–H bond decreases. Thus the E–H bond can break easily to produce H_2 gas which acts as a reducing agent. As the size of Bi atom is lnogest, therefore, Bi–H bond is the weakest amongst the hydrides of elements of group 15 and hence, BiH_3 is the strongest reducing agent.

Sol.2 Nitrogen has little tendency for catenation due to repulsion between non-bonded electron pairs.

The N–N bond is weaker than the single P–P bond due to high inter electronic repulsion of the non-bonding electrons in N2 owing to small bond length, therefore, the catenation property is weaker in nitrogen as compored to phosphorus.

Sol.3 (i) $I_2 + 10NHO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(ii) $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$

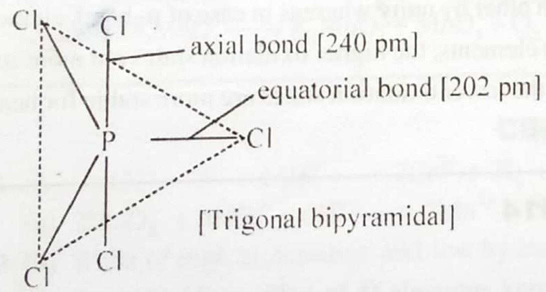
Sol.4 

[Peroxodisulpharic acid]

CBSE 2009

Sol.1 due to resonance.

CBSE — The p-Block Elements

Sol.2 

[Trigonal bipyramidal]

Sol.3 The eletronegativity of N is much higher than that of P. So, NH_3 undergoes extensive H-bonding and hence, it exists as an associated molecule. To break these additional bonds, the large amount of energy is required while pH_3 does not form H–bond and hence, exists as discrete molecule.

So.4 Since, Bi in +5 oxidation state has a tendency to reduce in to more stable +3 osidation state by the acceptance of two electrons and hence acts as a strong oxidising agent.

$$Bi^{5+} + 2e \longrightarrow Bi^{3+}$$

In contrast sb in +5 Oxidation state is more stable than its +3 Oxidation state. Therefore, of electrons than Bi5+. Hence, Bi(v) is a stronger oxidising agent than sb(v).

Sol.5 Due to decreasing electronegativity of central atom lone pair scatter out lone pair is not available

Sol.6 $NH_3 + NaOCl \longrightarrow 2NaONH_3 + Cl_2$