Chapter - 7

Anomalous behaviour of first member of p-Block Elements

VSA QUESTIONS (1 - MARK QUESTIONS)

1. In group 15 elements, there is considerable increase in covalent radius from N to P but small increase from As to Bi. Why?

   [**Hint :** Due to completely filled d- and / or f-orbitals in As, Sb and Bi.

2. The tendency to exhibit – 3 oxidation state, decreases down the group in group 15 elements. Explain.

   [**Hint :** Due to increase in size and decrease in electronegativity down the groups].

3. Maximum covalence of Nitrogen is '4' but the heavier elements of group 15 show covalence greater than '4'. Why?

4. Nitrogen exists as a diatomic molecule with a triple bond between the two atoms, whereas the heavier elements of the group do not exist as E_2 at room temperature. Assign a reason.

   [**Hint :** $p_\pi - p_\pi$ multiple bonds are formed by N due to its small size.]

5. The ionization enthalpies of group 15 elements are higher than those of corresponding members of group 14 and 16 elements. Assign the reason.

6. The boiling point of PH_3 is lesser than NH_3. Why?

7. NO_2 dimerises to form N_2O_4. Why?

   [**Hint :** Due to presence of odd electron on N]

8. Draw the structure of N_2O_5 molecule.

9. How does ammonia solution react with Ag^+ (aq)? Write the balanced chemical equation.

10. Why does NH_3 forms intermolecular hydrogen bonds whereas PH_3 does not?

    [**Hint :** Due to strong electronegativity, small size of Nitrogen atom and presence of lone pair of electrons on N atom]

11. Write disproportionation reaction of H_3PO_3?

12. How does NH_3 acts as a complexing agent?

    [**Hint :** Metal hydroxides are dissolved in excess of NH_4OH. Ammonia acts as a Lewis base].

13. Why HF is the weakest acid and HI is the strongest.

    Hint : Ka : (HF) = 7×10^{-4} (HI) = 7×10^{11}

Intermolecular H–bonds in H–F and high bond dissociation enthalpy of H–F makes it weakest and weak bond in H–I makes it strogest.

14. Explain why halogens are strong oxidising agents.

    [**Hint :** Ready acceptance of electron due to more negative eletron gain enthalpy.]

15. Why is Bi(V) a stronger oxidant than Sb(V)?

    [**Hint :** +3 oxidation state is more stable than +5 oxidation state in Bi].

16. Why SF_4 is easily hydrolysed, whereas SF_6 is resistant to hydrolysis?

    [**Hint :** Water molecule can not attack ‘S‘ atom due to steric hinderance and ‘S’ atom is also coordinately saturated in SF_6 molecule.]

17. Bond dissociation enthalpy of F_2 is less than that of Cl_2. Why?

18. Write the reaction of PCl_5 with heavy water.

    [**Hint :** $PCl_5 + D_2O \rightarrow POCl_3 + 2DCl$]

19. How many P – O – P bonds are there in cyclotrimetaphosphoric acid?

    [**Hint :** 3 bonds]

20. In group 16, the stability of +6 oxidation state decreases and that of +4 oxidation state increases down the group. Why?

    [**Hint :** due to inert pair effect]

21. Why we can not prepare HBr by heating KBr with sulphuric acid.

    [**Hint :** As HBr readily reduces H_2SO_4 forming Br_2]

24. Fluorine exhibit only –1 oxidation state whereas other halogens exhibit +ve oxidation states also. Explain.

25. Arrange the following oxoacids of chlorine in increasing order of acidic strength.

    HOCl, HOClO, $HOClO_3$, $HOClO_3$

*26. The majority of known noble gas compounds are those of Xenon. Why?

*27. “Hypophosphorus acid is a good reducing agent.” Justify with an example.

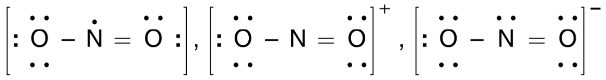
    [**Hint :** $4AgNO_3 + H_3PO_2 + 2H_2O \rightarrow 4Ag + HNO_3 + H_3PO_4$.

*28. Draw the structure of $H_4P_2O_7$ and find out its basicity?

    [**Hint :** Tetrabasic]

*29. Arrange the following triatomic species in the order of increasing bond angle.

NO_2, NO_2^+, NO_2^-

[**Hint :** 
$$\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - \overset{\cdot}{N} = \overset{\cdot\cdot}{O}:\right], \left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - N = \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\right]^{+}, \left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - \overset{\cdot\cdot}{N} = \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\right]^{-}$$

NO_2 has one non-bonding electron, NO_2^- has two non-bonding electrons, NO_2^+ has no non-bonding electron on N atom. Bond angle of $\overset{+}{NO}_2$ is maximum that of NO_2^- minimum].

30. With what neutral molecule ClO^- is isoelectronic?

31. Draw the structure of $H_2S_2O_8$ and find the number of S–S bond if any.

32. What is cause of bleaching action of chlorine water? Explain it with chemical equation?

[**Hint :** Formation of nascent oxygen]

*33. Electron gain enthalpy of fluorine is more negative than that of chlorine.

[**Hint. :** Due to small size of F atom, there are strong interelectronic repulsions in the relatively smaller 2p orbitals of fluorine. So the incoming electron does experience less attraction than in Cl]

*34. Which one of the following is not oxidised by O_3. State the reason.
KI, $FeSO_4$, K_2MnO_4, $KMnO_4$

[**Hint. :** $KMnO_4$ since Mn is showing maximum oxidation state of +7.]

SA (I) TYPE QUESTIONS (2 - MARK QUESTIONS)

2. Why is red phosphorus denser and less chemically reactive than white phosphorus?

3. Give chemical reaction in support of the statement that all the bonds in PCl_5 molecule are not equivalent.

[**Hint :** $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

4. Account for the following :

(a) XeF_2 has linear structure and not a bent structure.

(b) Phosphorus show marked tendency for Catenation.

5. Draw the structures of BrF_3, $XeOF_4$, XeO_3 using VSEPR theory.

6. Write the conditions that favour the formation of ammonia gas along with the reactions involved in Haber's Process.

7. Write the chemical equations of the following reactions

   (a) Glucose in heated with conc. H_2SO_4.

   (b) Sodium nitrate is heated with conc. H_2SO_4.

Complete the following reactions :

8. (i) $(NH_4)_2\ Cr_2O_7 \xrightarrow{\text{heat}}$

   (ii) $N_4H\ Cl\ (aq) + NaNO_2\ (aq) \longrightarrow$

9. (i) $NH_2CONH_2 + H_2O \longrightarrow$

   (ii) $FeCl_3\ (aq) + NH_4OH \longrightarrow$

10. (i) $Ca_3\ P_2 + H_2\ O\ (l) \longrightarrow$

   (ii) $I_2 + HNO_3\ (conc.) \longrightarrow$

11. (i) $Ba(N_3)_2 \xrightarrow{\text{heat}}$

   (ii) $4H_3PO_3 \xrightarrow{\text{heat}}$

12. (i) $PH_4I + KOH \longrightarrow$

   (ii) $HgCl_2 + PH_3 \longrightarrow$

13. (i) $PCl_3 + 3H_2O \longrightarrow$

   (ii) $S + H_2SO_4\ (conc.) \longrightarrow$

14. (i) $Al_2O_3(s) + NaOH\ (aq) + H_2O(l) \longrightarrow$

(ii) $HCl + O_2 \xrightarrow{CuCl_2}$

15. (i) $Ca(OH)_2 + Cl_2 \longrightarrow$

(ii) $XeF_4 + H_2O \longrightarrow$

16. (i) $Na_2SO_3 + Cl_2 + H_2O \longrightarrow$

(ii) $NaHCO_3 + HCl \longrightarrow$

17. (i) $XeF_6 + H_2O \xrightarrow[\text{hydrolysis}]{\text{Complete}}$

(ii) $XeF_6 + H_2O \xrightarrow[\text{hydrolysis}]{\text{Partial}}$

18. (i) $NO_3^- + Fe^{2+} + H^+ \longrightarrow$

(ii) $Zn + HNO_3\ (dil) \longrightarrow$

19. (i) $Zn + HNO_3\ (conc) \longrightarrow$

(ii) $P_4 + HNO_3\ (conc) \longrightarrow$

20. (i) $NH_3 + O_2 \xrightarrow{Pt/Rh}$

(ii) $P_4 + NaOH + H_2O \longrightarrow$

21. (i) $P_4 + SOCl_2 \longrightarrow$

(ii) $P_4 + SO_2Cl_2 \longrightarrow$

22. (i) $PbS + O_3 \longrightarrow$

(ii) $KI + H_2O + O_3 \longrightarrow$

23. (i) $MnO_4^- + SO_2 + H_2O \longrightarrow$

(ii) $\underset{\text{(dil)}}{Zn + HNO_3} \longrightarrow$

24. (i) NH_3 (Excess) + $Cl_2 \longrightarrow$

(ii) $NH_3 + Cl_2$ (Excess) $\longrightarrow$

25. (i) Cl_2 + NaOH (cold and dil) $\longrightarrow$

(ii) Cl_2 + NaOH (hot & conc) $\longrightarrow$

26. (i) $Fe + HCl \longrightarrow$

(ii) $Cl_2 + F_2$ (Excess) $\longrightarrow$

27. (i) $U + ClF_3 \longrightarrow$

(ii) $FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow$

28. (i) What is the covalency of N in N_2O_5?

(ii) Explain why phosphorus forms pentachloride whereas nitrogen and bismuth do not?

29. (i) The acidic character of hydrides of group 15 increases from H_2O to H_2Te. Why?

(ii) Dioxygen is a gas while sulphur (S_8) is a solid. Why?

30. (i) Interhalogen compounds are more reactive than halogens except F_2. Why?

(ii) Give one important use of ClF_3.

31. (i) Write the composition of bleaching powder.

(ii) What happens when NaCl is heated with conc. H_2SO_4 in the presence of MnO_2. Write the chemical equation.

32. Arrange the following in the decreasing order of their basicity. Assign the reason :

PH_3, NH_3, SbH_3, AsH_3, BiH_3.

*33. A colourless and a pungent smelling gas which easily liquifies to a colourless liquid and freezes to a white crystalline solid, gives dense white fumes with ammonia. Identify the gas and write the chemical equation for its laboratory preparation. [**Hint :** HCl]

*34. Complete following disproportionation reactions.

(a) $P_4 + NaOH + H_2O \longrightarrow$

(b) $HNO_2 \xrightarrow{H^+}$

35. Arrange the following trichlorides in decreasing order of bond angle NCl_3 PCl_3, $AsCl_3$, $SbCl_3$

36. Suggest reason why only known binary compounds of noble gases are fluorides and oxides of Krypton, Xenon.

[**Hint :** F and O are most electronegative elements. Kr and Xe both have low Ionisation enthalpies.]

37. Which fluorinating agent are oftenly used instead of F_2? Write two chemical equations showing their use as fluorinating agents.

[**Hint :** $BrF_5 + 3H_2O \rightarrow HBrO_3 + 5HF$

$2IF_7 + SiO_2 \rightarrow 2IOF_5 + SiF_4$]

38. (a) Hydrolysis of XeF_6 is not regarded as a redox reaction. Why?

(b) Write a chemical equation to represent the oxidising nature of XeF_4.

[**Hint :** (b) $XeF_4 + 2H_2 \rightarrow Xe + 4HF$)]

39. Write Chemical equation :

(a) XeF_2 is hydrolysed

(b) PtF_6 and Xenon are mixed together.

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

1. (i) How is HNO_3 prepared commercially?

   (ii) Write chemical equations of the reactions involved.

   (iii) What concentration by mass of HNO_3 is obtained?

2. (i) How does O_3 react with lead sulphide? Write chemical equation.

   (ii) What happens when SO_2 is passed in acidified $KMnO_4$ solution?

   (iii) SO_2 behaves with lime water similar to CO_2.

3. Assign reason for the following :

   (i) Sulphur in vapour state exhibits paramagnetism.

   (ii) F_2 is strongest oxidising agent among halogens.

   (iii) In spite of having same electronegativity, oxygen forms hydrogen bond while chlorine does not.

4. Give appropriate reason for each of the following :

   (i) Metal fluorides are more ionic than metal chlorides.

   (ii) Perchloric acid is stronger than sulphuric acid.

   (iii) Addition of chlorine to KI solution gives it a brown colour but excess of Cl_2 makes it colourless.

   [Hint :

   (i) According to Fajan's Rule, bigger ions more are polarised than the smaller ion by a particular cation.

   (ii) ClO_4^- is more resonance stabilised than SO_4^{2-} since dispersal of negative charnge is more effective in ClO_4^- as compared with SO_4^{2-}

   (iii) $2KI + Cl_2 \rightarrow 2KCl + I_2$

   Excess $5Cl_2 + I_2 + 6H_2O \rightarrow 2HIO_3 + 10\ HCl$ (Colourless).

5. Explain why :

   (i) No chemical compound of helium is known.

   (ii) Bond dissociation energy of fluorine is less than that of chlorine.

   (iii) Two S–O bonds in SO_2 are identical.

6. Out of the following hydrides of group 16 elements, which will have :

   (i) H_2S (ii) H_2O (iii) H_2Te

(a) lowest boiling point

(b) highest bond angle

(c) highest electropositive hydrogen.

7. (i) How is XeO_3 prepared from XeF_6? Write the chemical equation for the reaction.

   (ii) Draw the structure of XeF_4.

8. (i) Thermal stability of hydrides of group 16 elements decreases down the group. Why?

   (ii) Compare the oxidising powers of F_2 and Cl_2 on the basis of bond dissociation enthalpy, electron gain ethalpy of hologens and hydration enthalpy of halide ions.

   (iii) Write the chemical equation for the reaction of copper metal with conc. HNO_3.

*9. An unknown salt X reacts with hot conc. H_2SO_4 to produce a brown coloured gas which intensifies on addition on copper turnings. On adding dilute ferrous sulphate solution to an aqueous solution of X and then carefully adding conc. H_2SO_4 along the sides of the test tube, a brown complex Y is formed at the interface between the solution and H_2SO_4. Identify X and Y and write the chemical equation involved in the reaction.
[**Hint :** X is NO_3^- salt].

10. Assign reason to the following :

    (i) Noble gases have large positive values of electron gain enthalpy.

    (ii) Helium is used by scuba divers.

11. Arrange the following in the order of the property indicated for each set–

    (a) F_2, Cl_2, Br_2, I_2 (Increasing bond dissociation energy).

    (b) HF, HCl, HBr, HI (decreasing acid strength).

    (c) NH_3, PH_3, ASH_3, SbH_3, BiH_3 (decreasing base strength).

    [Hint :

    (a) F_2 has exceptionally low bond dissociation enthalpy. Lone pairs in F_2 molecule are much closer to each other than in Cl_2 molecule. Larger electron–electron repulsions among the lone pairs in F_2 molecule make its bond dissociation enthalpy exceptionally low.

    (b) Depends upon H–X bond dissociation enthalpy as the size of atom increases, bond dissociation enthalpy of H–X decreases.

(c) Electron availability on the central atom 'E' in EH_3 decreases down the group.

*12. A transluscent while waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B), Allotrope (A) on reaction with very dilute aqueous NaOH liberates a highly poisonous gas (C) having a rotten fish smell, with excess of chlorine forms D which hydrolyses to form compound (E). Identify the compounds (A) to (E).

A : White phosphorus, B : Red phosphorus, C : PH_3, D : PCl_3, E : H_3PO_4

13. Write balanced equation for the following reactions :

(a) Zn is treated with dilute HNO_3.

(b) NaCl is heated with H_2SO_4 in the presence of MnO_2.

(c) Iodine is treated with conc. HNO_3.

14. X_2 is a greenish yellow gas with pungent offensive smell used in purification of water. It partially dissolves in H_2O to give a solution which turns blue litmus red. When X_2 is passed through NaBr Solution, Br_2 is obtained.

(a) Identify X_2, name the group to which it belongs.

(b) What are the products obtained when X_2 reacts with H_2O? Write chemical equation.

(c) What happens when X_2 reacts with hot and conc. NaOH? Give equation.

16. Assign the appropriate reason for the following:

(a) Nitrogen exists as diatomic molecule and phorphorous as P_4, Why?

(b) Why does $R_3P = 0$ exist but $R_3N = 0$ does not ? (R = an alkyl group).

(c) Explain why fluorine forms only one oxoacid, HOF.

[Hint :

(a) Due to its small size and high electronegativity N forms $p\pi - p\pi$ multiple bond ($N \equiv N$). whereas P does not form $p_\pi - p_\pi$ bonds but forms P – P single bond.

(b) Due to the absence of d-orbitals, N cannot expand its covalence beyond four.

In $R_3N = 0$, N should have a covalence of 5 so the compound $R_3N = 0$ does not exist since maximum covalence shown by N cannot exceed 4.

(c) F does not form oxoacids in which the oxidation state of F would be +3, +5, +7, it forms one oxoacid, because of unavailability of d orbitals in its valence shell.

LONG ANSWER TYPE QUESTIONS (5 - MARK QUESTIONS)

1. How is PH_3 prepared in the laboratory? How is it purified? How does the solution of PH_3 in water react on irradiation with light and on absorption in $CuSO_4$? How can you prove that PH_3 is basic in nature?

   Write the chemical equations for all the reactions involved.

2. Assign a possible reason for the following :

   (a) Stability of +5 oxidation state decreases and that of +3 oxidation state increases down the group 15 elements.

   (b) H_2O is less acidic than H_2S.

   (c) SF_6 is inert while SF_4 is highly reactive towards hydrolysis.

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

   (e) Noble gases have comparatively large size in their respective periods.

3. (a) How is XeF_6 prepared from the XeF_4? Write the chemical equation for the reaction.

   (b) Deduce the structure of XeF_6 using VSEPR theory.

   (c) How does XeF_2 reacts with PF_5?

   (d) Give one use each of helium and neon.

   (e) Write the chemical equation for the hydrolysis of XeF_4.

4. (a) Why does nitrogen show anomalous behaviour? Discuss the trend of chemical reactivity of group 15 elements with.

   (a) oxygen (b) halogens (c) metals

   (b) H_3PO_3 is a dibasic acid. Why?

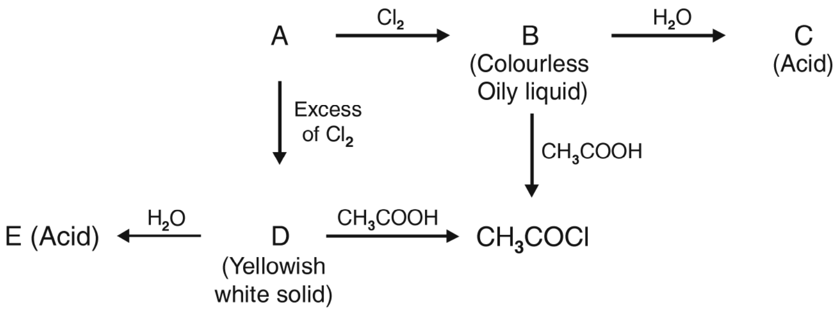
5. (a) Arrange the following in the order of their increasing acid strength.

   (a) Cl_2O_7, SO_2, P_4O_{10}

   (b) How is N_2O gas prepared? And draw its structure.

   (c) Give one chemical reaction to show O_3 is an oxidising agent.

*6. Identify A, B, C, D and E in the following sequence of reactions



Complete the reactions of the above mentioned sequence.

[**Hint :** A is P_4].

*7. A white waxy, translucent solid, M, insoluble in water but soluble in CS_2, glows in dark. M dissolves in NaOH in an inert atmosphere giving a poisonous gas (N). Also M catches fire to give dense white fumes of Q :

(a) Identify M, N and Q and write the chemical equations of the reactions involved.

(b) M exists in the form of discrete tetrahedral molecules. Draw its structure.

(c) M on heating at 573 K is changed into other less reactive form, Q, which is non-poisonous, insoluble in water as well as in CS_2 and does not glow in dark, Identify Q and draw its structure.

8. Write the structure of A, B, C, D and E in the following sequence of reactions :

$$NH_3 + O_2 \xrightarrow{Pt/Rh} A + H_2O$$

$$A + O_2 \longrightarrow B \text{ (brown fumes)}$$

$$B + H_2O \longrightarrow C + A \text{ (C is an oxoacid)}$$

$$C + I^- \longrightarrow D \text{ (Violet vapours)}$$

Complete reactions of the above mentioned sequence and name the process by which ‘C’ is obtained.

[**Hint. :** A is NO and Ostwald process for the manufacture of HNO_3].

9. Give reason for each of the following :

   (a) NH_3 is more basic than PH_3.

   (b) Ammonia is a good complexing agent.

   (c) Bleaching by SO_2 is temporary.

   (d) PCl_5 is ionic in solid state.

   (e) Sulphur in vapour state exhibits paramagnetism.

10. Knowing the electrons gain enthalpy value for $O \rightarrow O–$ and $O^- \rightarrow O^{2-}$ as -141 and 720 kJ mol^{-1} respectively, how can you account for the formation of large number of oxides having O^{2-} species and not O^-?

    [**Hint :** Latlice enthalpy of formation of oxides having O^{2-} more than compensates the second $\Delta_{eg}H$ of oxygen.