Unit - 7

Anomalous behaviour of first member of p-Block Elements

Anomalous behaviour of first element in the p-block elements is attributed to small size, large (charge/radius) ratio, high ionization enthapy, high electronegativity and unavailability of d-orbitals in its valance shell.

Consequences :

1. The first element in p-block element has four valence orbitals i.e. one 2s and three 2p, Hence maximum covalency of the first element in limited to four. The other elements of the p-block elements have vacant d-orbitals in their valence shell, e.g. elements of the third period have nine (9) one 3s, three 3p and five three 3d orbitals. Hence these show maximum covalence greater than four. Following questions can be answered -

   (i) Nitrogen (N) does not from pentahalide while P froms PCl_5, PF_5, and PF_6^-. Why?

   (ii) Sulphur (S) forms SF_6 but oxygen does not form OF_6. Why?

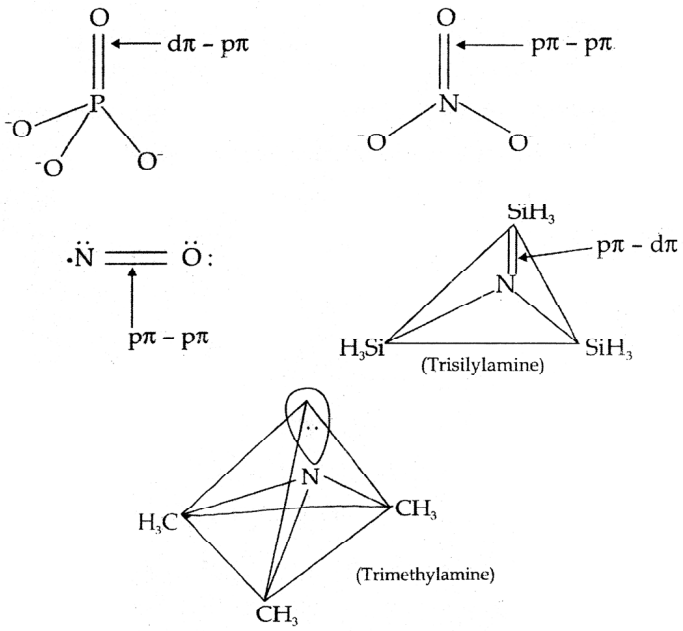
   (iii) Though nitrogen forms pentoxide but it does not form pentachloride. Explain. Why?

   (iv) Fluorine forms only one oxoacid while other halogens form a number of oxoacids. Why?

(2) The first member of p-block elements displays greater ability to from $p\pi$-$p\pi$ bond (s) with itself, (e.g., C = C, C ≡ C, N = N, N ≡ N) and with the other elements of second period (e.g., C = O, C ≡ N, N = O) compared to the subsequent members of the group.

This is because p-orbitals of the heavier members are so large and diffuse that they cannot have effective sideways overlapping. Heavier members can form $p_\pi - d_\pi$ bonds with oxygen.

Nitrogen rarely forms pπ–dπ bonds with heavier elements as in case of trisilylamine $(SiH_3)_3N$.



Now, the following questions can be explained using the above reasoning-

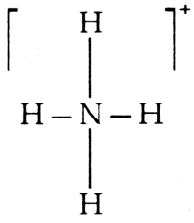
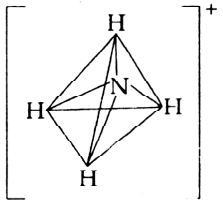
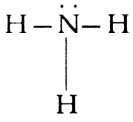
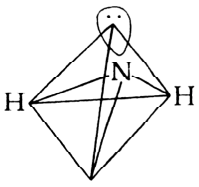
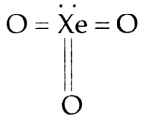
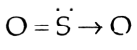
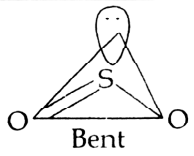
(i) Nitrogen forms N_2 but phosphorus forms P_4 at room temperature. Why?

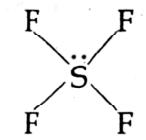
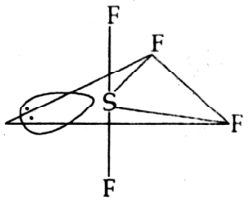
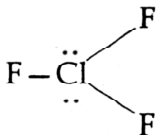
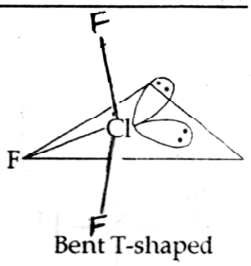
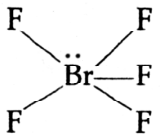
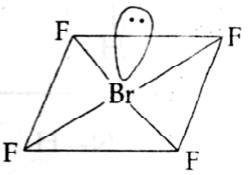
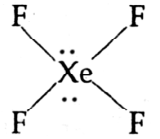
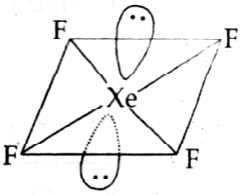
(ii) Oxygen forms O_2 but sulphur exists as S_8. Why?

(iii) Explain why $(CH_3)_3$ P = O is known but $(CH_3)_3$ N = O is not known.

3. Due to small size and high electronegativity and presence of lone pair(s) of electrons, elements N, O, F when bonded to hydrogen atom, forms intermolecular hydrogen bonds which are stronger than other intermolcular forces. This results in exceptionally high m.p. and b.p. of the compounds having N–H/O–H/F–H bonds.

Shapes of some molecular/ionic species and hybridisation state of central atom.

Lewis structure	lone pairs + bond pairs and hydridi-sation of central atom	Electron-pair geometry	Shape of species
	0 + 4 = 4 (sp^3)	Tetrahedral	 Tetrahedral
	1 + 3 = 4 (sp^3)	Tetrahedral	 Pyramidal
	1 + 3 = 4 (sp^3)	Tetrahedral	Pyramidal
	1 + 2 = 3 (sp^2)	Trigonal planner	 Bent

O = C = O	0 + 2 = 2 sp^2	Linear	Linear
	1 + 4 = 5 (sp^3d)	Trigonal-bipyramidal	 Sea-saw
	2 + 3 = 5 (sp^3d)	Trigonal-bipyramidal	 Bent T-shaped
	1 + 5 = 6 (sp^3d^2)	Octahedral	 Square Pyramidal
	2 + 4 = 6 (sp^3d^2)	Octahedral	 Square Planar

Note: Multiple bond is treated as single super pair. A π-bond shortens the bond length without affecting the geometry.

The state of hybridisation of the central atom is determined by sum of bond pairs and lone pair (s) if present arount the central atom in a molecule/ion.

Isostructural species have same number of bond pairs and lone pairs if present around the central atom in a molecule/ion. Thus, they have the same geometry/shape/structure and the same hybridisation scheme. For example ICl_4^- / XeF_4, BrO_3^-/XeO_3, BH_4^-/NH_4^+ are the pairs oi isostructural species.

Inert pair effect : Due to poor shielding effect of intervening d and/ or f–electrons, the effective nuclear charge is increased. This increased nuclear charge holds the ns^2 electrons of heavier elements to participate in bonding and the tendency of ns^2 electrons to take part in bonding is more and more restricted down the group. Consequently, more stable lower oxidation state which is two units less than higher oxidation state becomes more and more stable than the higher oxidation state. For example, following questions can be exptalend with the help of inert pair effect.

(a) For N and P, + 5 oxidation state is more stable than + 3 oxidation state but for Bi, + 3 oxidation state is more stable than + 5. Explain why?

(b) $NaBiO_3$ is a strong oxidising agent. Why?
(**Hint :** Bi(v) is least stable O.S.).

(c) In group 16 stability of + 6 oxidiation state decreases and the stability of + 4 oxidation increases down the group. Why?

(d) SO_2 acts as reducing agent. Explain why?

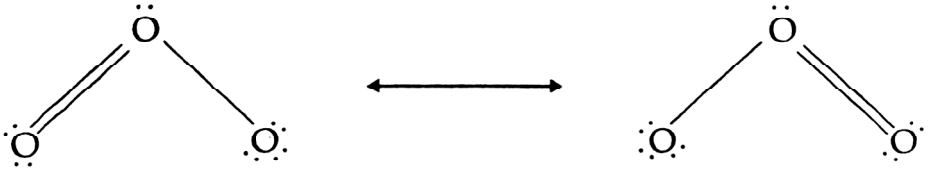
(e) Why is BrO_4^- a stronger oxidising agent than ClO_4^- ?

[**Hint :** It is because + 7 oxidation state in less stable in BrO_4^- due to which Br – O bond becomes weaker.]

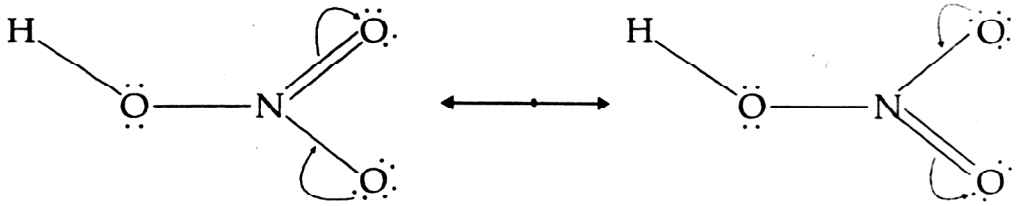
(f) $BiCl_5$ is highly unstable.

(g) The stability of highest oxidation state of 4p element is less than those of 3p and 5p elements of the same group?

Bond Length : Resonance averages bond lengths. The two oxygen–oxygen bond length are identical in the O_3 molecule because it is resonance hybrid of two cannonical forms.



In case of HNO_3, two nitrogen–oxygen bonds are identical and smaller than the third nitrogen–oxygen bond.

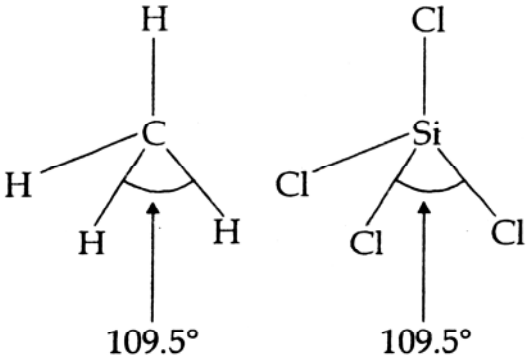


Now the following questions can be expained on the basis of this concept.

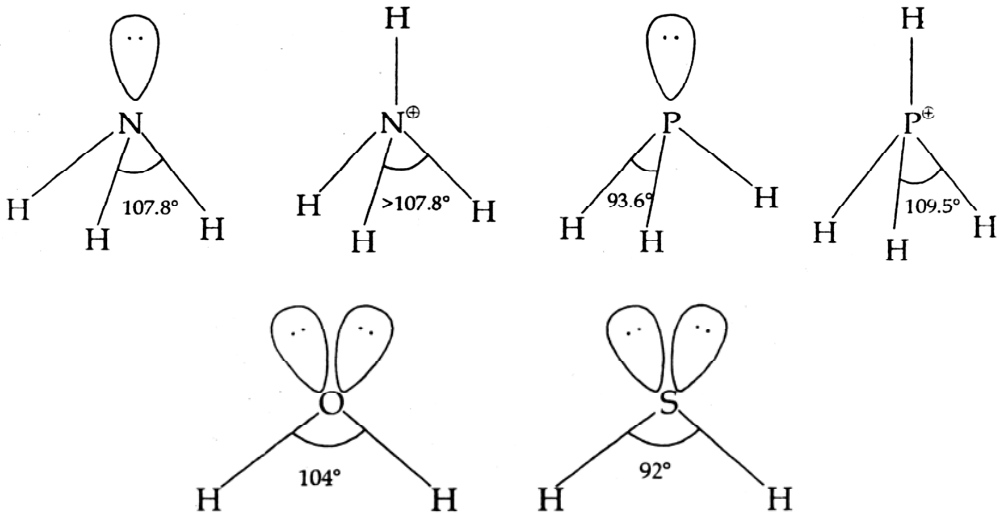
(i) In SO_2, the two sulphur-oxygen bonds are identical. Explain why?

(ii) In NO_3^- ion all the three N–O bonds are identical. Why?

Bond angle : In regular structures (where no lone pairs are present in the valence shell of the central atom in a molecule/ion), the bond angle does not depend upon the size/electronegativity of the central or terminal atoms.



In presence of lone pair(s) on the central atom, the geometry is distorted and the bond angle in changed.



Comparison of HNH and HPH bond angles

Since N is more electronegative than P, the bonding electron pair of N–H bond will shift more towards N atom than the bonding electron pair of P–H bond would shift towards P atom. This results in more bond pair-bond pair repulsion in NH_3

molecules than PH_3 molecule. Because of lp-bp repulsion the N–H are pushed closer to a less extent than in PH_3, Consequently, HNH bond angle is greater than HPH angle.

Now the following questions can be explained using the above mentioned concept.

(i) Bond angle in PH_4^+ ion is higher than in PH_3. Why?

(ii) H–O–H bond in H_2O in greater than H–S–H angle in H_2S. Why?

(iii) Cl–P–Cl bond angle in PCl_3 (100°) is less than F–N–F bond angle in NF_3 (102°). Explain why?

(iv) Bond angle in OF_2 (105°) molecule is less than in OCl_2 (110°). Why?

Boiling and melting points of hydrides depends upon the molar mass (or surface area) of molecules. More the molar mass, the higher in the m.p. and b.p. Hydrides forming intermolecular hydrogen bonds have exceptionally high m.p. and b.p. since intermolecular hydrogen bonds are stronger than the Van der waals forces.

Increasing order of melting point and boiling point of hybrides is as given below :

$PH_3 < AsH_3 < SbH_3 < NH_3$; Melting point

$PH_3 < AsH_3 < NH_3 < SbH_3$; Boiling point

$H_2S < H_2Se < H_2Te < H_2O$; Melting point and Boiling point

HCl < HBr < HI < HF ; Boiling point

HCl < HBr < HF < HI ; Melting point

Thermal stability, reducing power and acid strength of hydrides depend upon bond dissociation enthalpy of E - H bond (E = group 15, group 16, and group 17 element). Due to the increase in size down the group, bond dissociation enthalpy of E - H bond decreases. Consequently, thermal stability, reducing power and acid strength of hydrides increases down the group.

The following questions can be explained using the above concepts.

Explain why :

(i) NH_3 has higher boiling point than PH_3.

(ii) H_2O is liquid and H_2S is gas or H_2S is more volatile than H_2O.

(iii) HE is weaker acid than HCl.

(iv) Among hydrogen halides, HI is the strongest reducing agent.

(v) H_2Te is more acidic than H_2S.

(vi) NH_3 is mild oxireducing agent while BiH_3 is the strongest reducing agent among the group-15 hydrides.

(vii) H_2S is weaker reducing agent than H_2Te.

Basic nature of hydrides EH_3 of group 15 elements

All the hydrides EH_3 has one lone pair of electron. In ammonia the lone pair of electron is present in, sp^3 hybrid orbital of the N-atom. The sp^3 hybrid orbital is directional and further N is more electronegtive than H, the bond pair of N - H is shifted towards N atom which further increases the electron density on N atom. In PH_3, the lone pair of electron is present in large and more diffuse 3s orbital which is non-directional. As a result PH_3 is less basic than NH_3 and basic character decreases down the group. NH_3 donates electron pair more readily than PH_3. $(SiH_3)_3N$ has less Lewis basic nature than that of $(CH_3)_3N$ because lone pair of electrons in p - orbital of N atom in $(SiH_3)_3N$ is transferred to the vacant d - orbital of Si atom forming $d\pi - p\pi$ fond.

COVALENT/IONIC CHARACTER OF HALIDES

Pentahalides are more covalent than trihalides since the element (E) in higher oridation state (+ 5) has more polarising power than element (E) in lower oxidation state (+ 3) in trihalides, Similarly $SnCl_4$, $PbCl_4$, $SbCl_5$ and UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

Following questions can be explained by using this concept. Explain why :

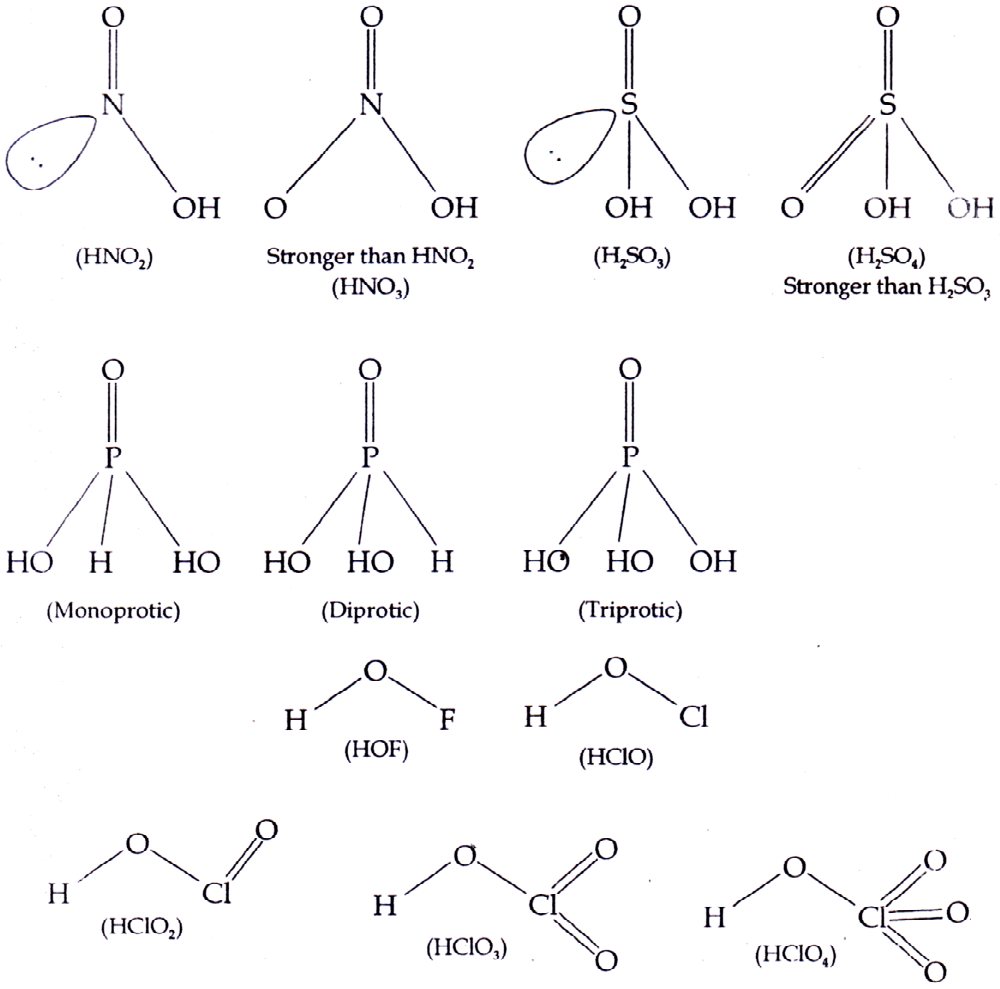
(i) $SnCl_2$ has more b.p. than $SnCl_4$.

(ii) $SbCl_5$ is more covalent than $SbCl_3$.

(iii) PCl_5 has lower boiling point than that of PCl_3.

Oxoacids of N, P and halogens :

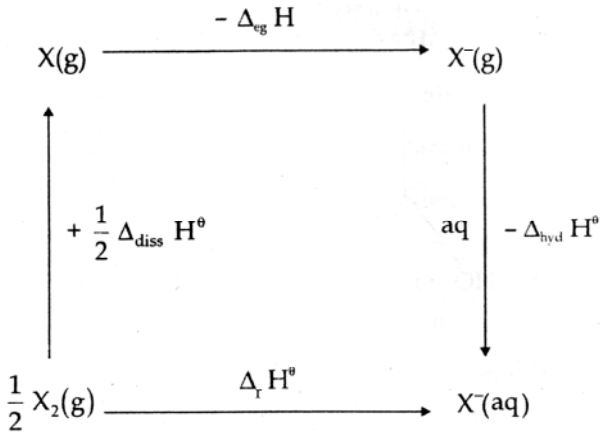
Strength of oxoacid depends upon the polarity of O–H bond which in turn, depends on the electron with drawing power (or electronegativity) of the element E. Strength of oxoacids increase if the number of oxygen atom bonded with E increases.



Strength of oxoacid of halogens in the same oxidation state depends on the electronegativity of the halogen. The more the electrongeativeity, stronger is the oxoacid.

Stength of oxoacid of a halogen in different oxidation state increases with the increase in oxidation state. This is because the stabilisation of the oxoanion increases with the number of the oxygen atoms bonded to the halogen atom. More the number of oxygen atoms, the more the dispersal of –ve charge present on the oxoanion and stronger will be the oxoacid.

Oxidising power of halogens :



The more negative the value of $\Delta rH^\theta = \frac{1}{2}\Delta_{diss}H^\theta - \Delta_{eg}H^\theta - \Delta_{hyd}H^\theta$, the higher will be oxidising property of the halogen and more positive will be standard reduction potential E^θ_{red} of the halogen.

Following questions can be explained on the basis of parameters e.g., $\Delta_{diss}H^\theta$, eg H^θ and $\Delta_{hyd}H^\theta$.

(i) Why does F_2 have exceptionally low bond dissociation enthaply?

(ii) Although electron gain entharpy of fluorine(F) is less negative as compared to chlorine. (Cl), Flunorine (F_2) is a stronger oxidising agent than Cl_2. Why?

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.

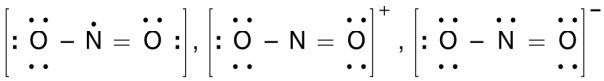
[**Hint :** $4AgNO_3 + H_3PO_2 + 2H_2O \rightarrow 4Ag + HNO_3 + H_3PO_4$.

*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 :** 

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 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) $(NH_4)_2\ Cr_2O_7 \xrightarrow{heat}$

(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) $Ba(N_3)_2 \xrightarrow{heat}$

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

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

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?

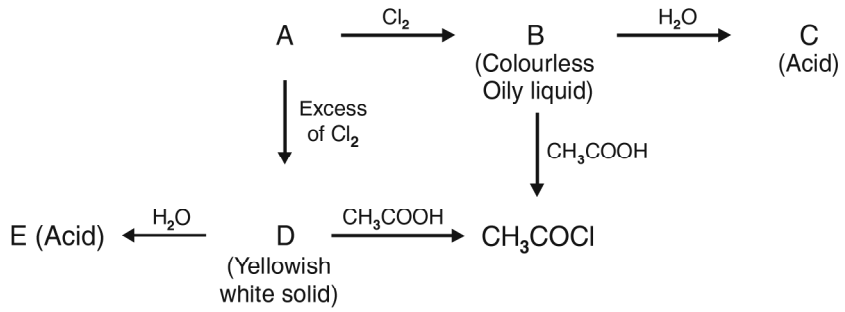
5. (a) Arrange the following in the order of their increasing acid strength.

   (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.