

UNIT 7

p-BLOCK ELEMENTS

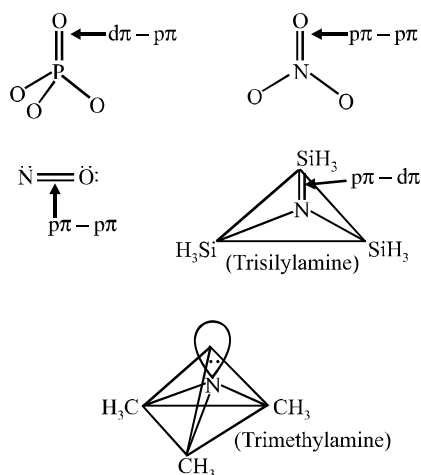
Anomalous behavior of first element in the p-block elements is attributed to small size, large (charge/radius) ratio, high ionization enthalpy, high electronegativity and unavailability of d-orbitals in its valence shell.

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 is limited to four. The other elements of the p-block have vacant d-orbitals in their valence shell, *e.g.*, three 3p and five three 3d orbitals. Hence, these elements show maximum covalence greater than four. Following questions can be answered :
 - (i) Nitrogen (N) does not form pentahalide while P forms 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. 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 form $\text{p}\pi\text{-p}\pi$ bond(s) with itself, (*e.g.*, $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{N}=\text{N}$, $\text{N}\equiv\text{N}$) and with the other elements of second period, for example, $\text{C}=\text{O}$, $\text{C}\equiv\text{N}$, $\text{N}=\text{O}$ 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 $\text{p}\pi\text{-d}\pi$ bonds with oxygen.

Nitrogen rarely forms $\text{p}\pi\text{-d}\pi$ bonds with heavier elements as in case of trisilylamine $(\text{SiH}_3)_3\text{N}$.



Now, the following questions can be explained using the above mentioned reasoning :

- (i) Nitrogen forms N_2 but phosphorus forms P_4 at room temperature. Why ?
 - (ii) Oxygen exists as O_2 but sulphur as S_8 . Why ?
 - (iii) Explain why $(CH_3)_3P=O$ is known but $(CH_3)_3N=O$ 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 hydrogen bonds which are stronger than other intermolecular forces. This results in exceptionally high m.p. and b.p. of the compounds having N-H/O-H/F-H bonds.

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 of isostructural species.

Inert pair effect: Due to poor shielding effect of intervening d and/or f-electrons, the effective nuclear charge increases. This increased nuclear charge holds the ns^2 electrons of heavier elements strongly 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. Following questions can be explained with the help of inert pair effect :

- (i) 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 ?
- (ii) $NaBiO_3$ is a strong oxidizing agent. Why ? [*Hint* : Bi (V) is least stable.]

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

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

(v) Why is BrO_4^- a stronger oxidizing agent than ClO_4^- ?

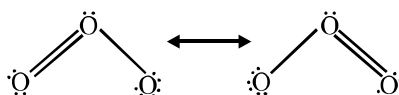
[Hint : It is because +7 oxidation state is less stable in BrO_4^- due to which Br – O bond becomes weaker.]

(vi) AsCl_5 is less stable than SbCl_5 .

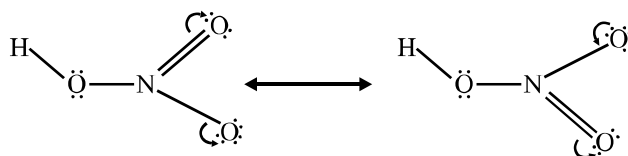
[Hint : More effective nuclear charge in As than Sb.]

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

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



In case of HNO_3 , two nitrogen-oxygen bonds are identical and smaller than the third nitrogen-oxygen bond. This is because the third N – OH bond is not involved in resonance.

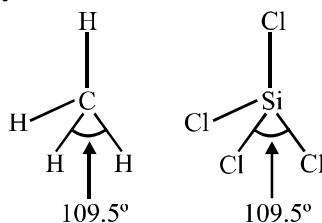


Now the following questions can be explained on the basis of this concept :

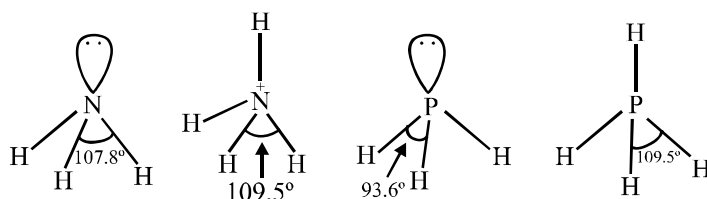
(i) In SO_2 , the two sulphur-oxygen bonds are identical. Explain why ?

(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 is 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 molecule than PH_3 molecule. Because of more lp-bp repulsion, the N–H bonds are pushed closer to a lesser 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 :

- Bond angle in PH_4^+ ion is higher than in PH_3 . Why ?
- H–O–H bond in H_2O is greater than H–S–H angle in H_2S . Why ?

Boiling and melting points of hydrides depends upon the molar mass (or surface area) of molecules. More the molar mass, the higher is 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 hydrides is as given below :

$\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$	Melting point
$\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3$	Boiling point
$\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{O}$	Melting point and boiling point
$\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$	Boiling point
$\text{HCl} < \text{HBr} < \text{HF} < \text{HI}$	Melting point

- NH_3 has higher boiling point than PH_3 .
- H_2O is liquid and H_2S is gas or H_2S is more volatile than H_2O .

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) HF is weaker acid than HCl.
- (ii) Among hydrogen halides, HI is the strongest reducing agent.
- (iii) H_2Te is more acidic than H_2S .
- (iv) NH_3 is mild reducing agent while BiH_3 is the strongest reducing agent among the group-15 hydrides.
- (v) H_2S is weaker reducing agent than H_2Te .

Basic nature of hydrides EH_3 of group 15 elements

All the hydrides EH_3 of group 15 elements has one lone pair of electrons. In ammonia, the lone pair of electrons is present in sp^3 hybrid orbital of the N-atom. The sp^3 hybrid orbital is directional and further N is more electronegative 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 electrons 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 . $(\text{SiH}_3)_3\text{N}$ has less Lewis basic nature than that of $(\text{CH}_3)_3\text{N}$ because lone pair of electrons in p-orbital of N atom in $(\text{SiH}_3)_3\text{N}$ is transferred to the vacant d-orbital of Si atom forming $\text{d}\pi\text{-p}\pi$ bond.

Covalent/Ionic Character of Halides

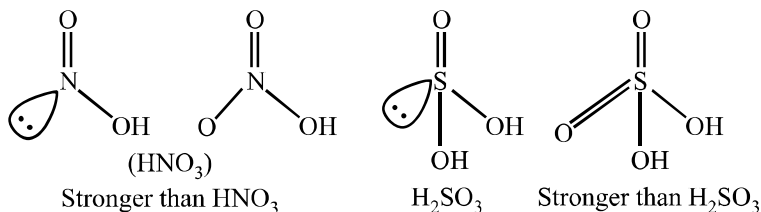
Pentahalides are more covalent than trihalides since the element (E) in higher oxidation state (+ 5) in pentahalides has more polarizing power than element (E) in lower oxidation state (+ 3) in trihalides, similarly, SnCl_4 , PbCl_2 , SbCl_3 and UF_4 respectively. Compounds having more ionic character have more m.p. and b.p. than the compounds having more covalent character.

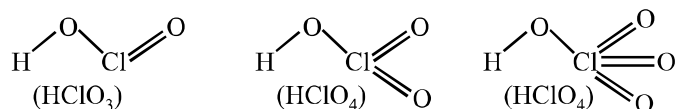
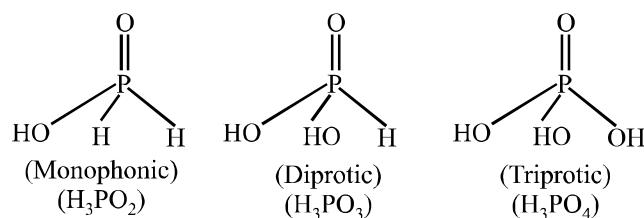
Following questions can be explained by using this concept.

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 :





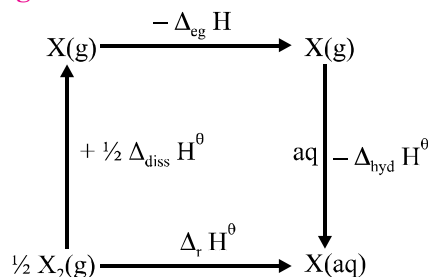
Strength of Oxo Acids

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

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

Strength of oxoacid of a halogen in different oxidation state increases with the increase in oxidation state. This is because the stabilization 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 $\Delta_{\text{r}} H^\theta = \frac{1}{2} \Delta_{\text{diss}} H^\theta - \Delta_{\text{eg}} H^\theta - \Delta_{\text{hyd}} H^\theta$ the higher will be oxidizing property of the halogen and more positive will be standard reduction potential E_{red}^θ of the halogen.

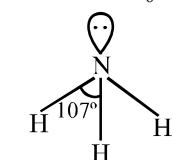
Following questions can be explained on the basis of parameters, like $\Delta_{\text{diss}} H^\theta$, $\Delta_{\text{eg}} H^\theta$ and $\Delta_{\text{hyd}} H^\theta$.

- (i) Why does F_2 have exceptionally low bond dissociation enthalpy ?
- (ii) Although electron gain enthalpy of fluorine (F) is less negative as compared to chlorine (Cl), Fluorine gas (F_2) is a stronger oxidizing agent than Cl_2 gas. Why ?

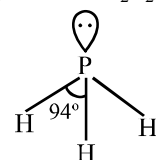
Some Important Reactions

- $(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$
- $FeCl_3(aq) + NH_4OH(aq) \rightarrow Fe_2O_3 \cdot xH_2O(s) + NH_4Cl(aq)$
- $Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$
- $AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]Cl$
- $2Pb(NO_3)_2 \xrightarrow{673\text{ K}} 4NO_2 + 4PbO + O_2$
- $4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$
- $3Cu + 8HNO_3(\text{dil.}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
- $Cu + 4HNO_3(\text{conc.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
- $4Zn + 10HNO_3(\text{dil.}) \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$
- $Zn + 4HNO_3(\text{conc.}) \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$
- $I_2 + 10HNO_3(\text{conc.}) \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$
- $S_8 + 48HNO_3(\text{conc.}) \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$
- $P_4 + 20HNO_3(\text{conc.}) \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$
- Chemistry of ring test :
 $NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$
 $[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$
- $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$
- $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$
- $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$
- $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
- $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 3HCl$
- $4H_3PO_3 \xrightarrow{\text{heat}} 3H_3PO_4 + PH_3$
- $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$
- $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
- $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$
- $2F_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$
- $X_2(g) + H_2O(l) \rightarrow HX(aq) + HXO(aq) \text{ (X = Cl, Br)}$
- $4I^-(aq) + 4H^+(aq) + O_2 \rightarrow 2I_2(s) + 2H_2O(l)$

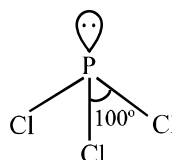
27. $\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$
28. $2\text{NaOH (dil)} + \text{X}_2 \xrightarrow{\text{Cold}} \text{NaX} + \text{NaOX} + \text{H}_2\text{O}$
29. $6\text{NaOH (conc)} + 3\text{X}_2 \xrightarrow{\text{heat}} 5\text{NaX} + \text{NaXO}_3 + 3\text{H}_2\text{O} \quad (\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2)$
30. $2\text{Ca(OH)}_2 + 2\text{Cl}_2 \rightarrow \text{Ca(OCl)}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$
31. $\text{NaCl} + \text{H}_2\text{SO}_4 \xrightarrow{\text{heat}} \text{NaHSO}_4 + \text{HCl}$
32. $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+[\text{PF}_6]^-$
33. $\text{XeF}_6 + \text{MF} \rightarrow \text{M}^+[\text{XeF}_7]^- \quad (\text{M} = \text{Na, K, Rb or Cs})$
34. $6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2$
35. $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$
36. $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$
37. $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$



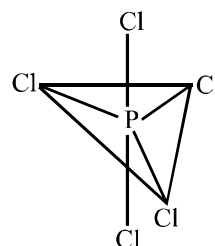
NH_3
 Sp^3 (Pyramidal)



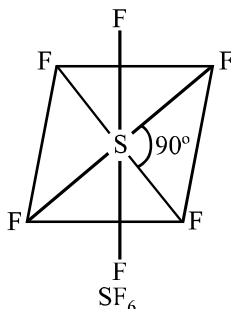
PH_3
 Sp^3 (Pyramidal)



Sp^3 (Pyramidal)
 PCl_3



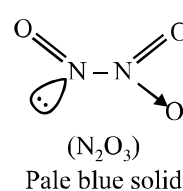
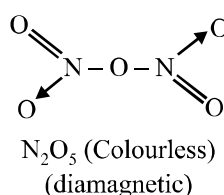
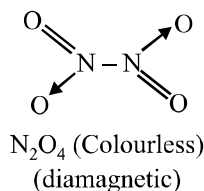
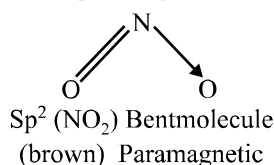
Sp^3d (Trigonalbipyramidal)

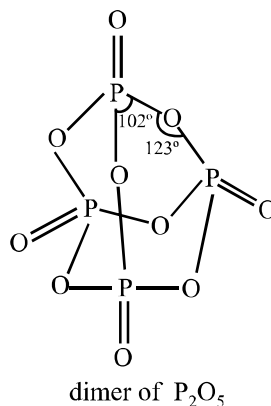
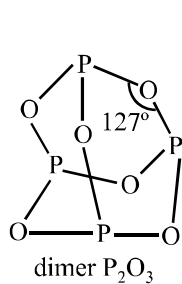


Sp^3d (octahedral)

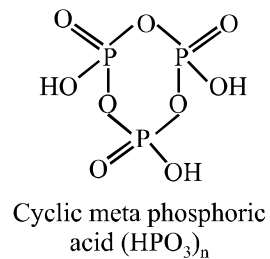
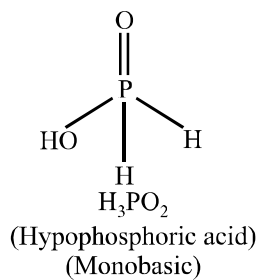
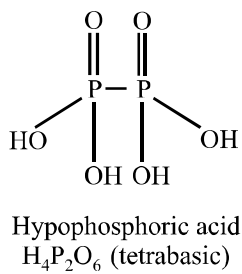
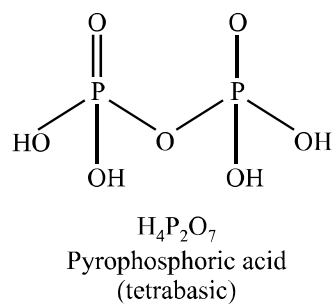
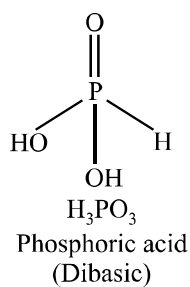
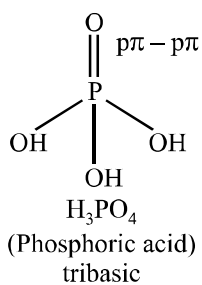
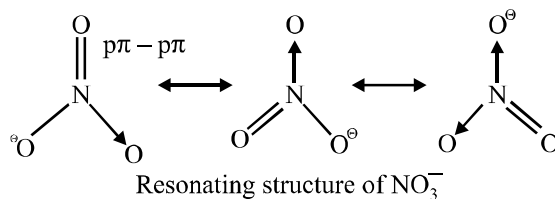
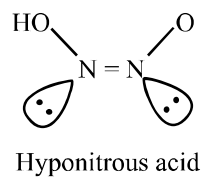
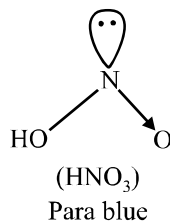
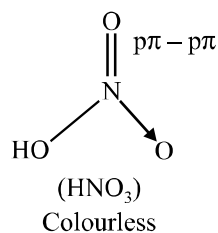
$\text{N} \equiv \text{N} \rightarrow \text{O}$
(N_2O) Colourless
Linear

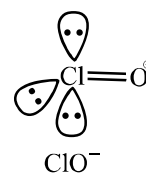
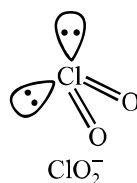
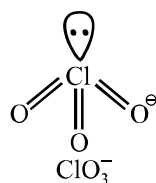
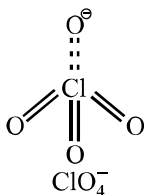
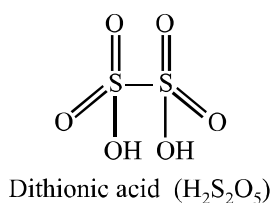
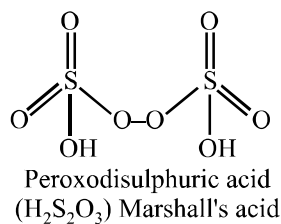
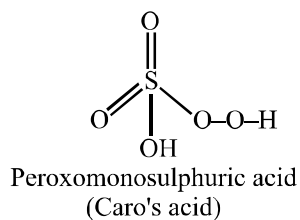
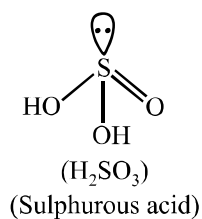
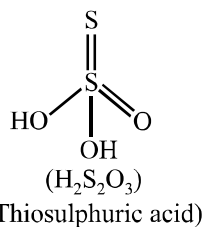
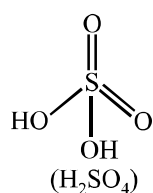
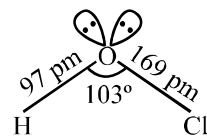
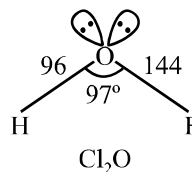
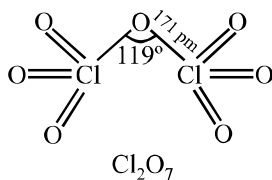
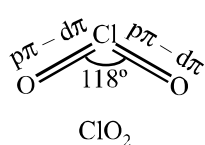
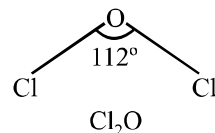
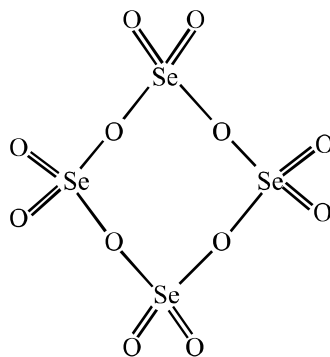
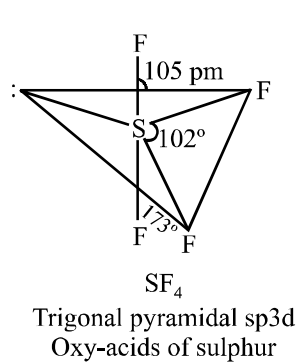
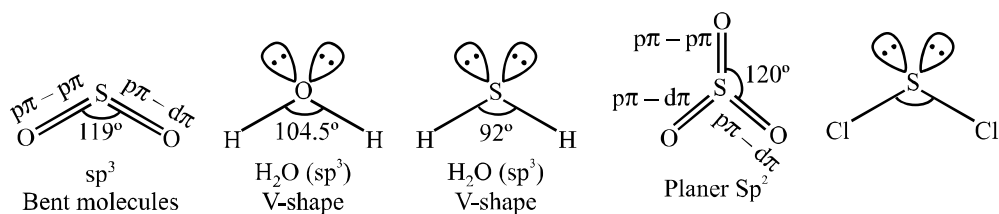
Oxides of Nitrogen
: $\text{N} = 0$
Nitric oxide (colourless)
paramagnetic

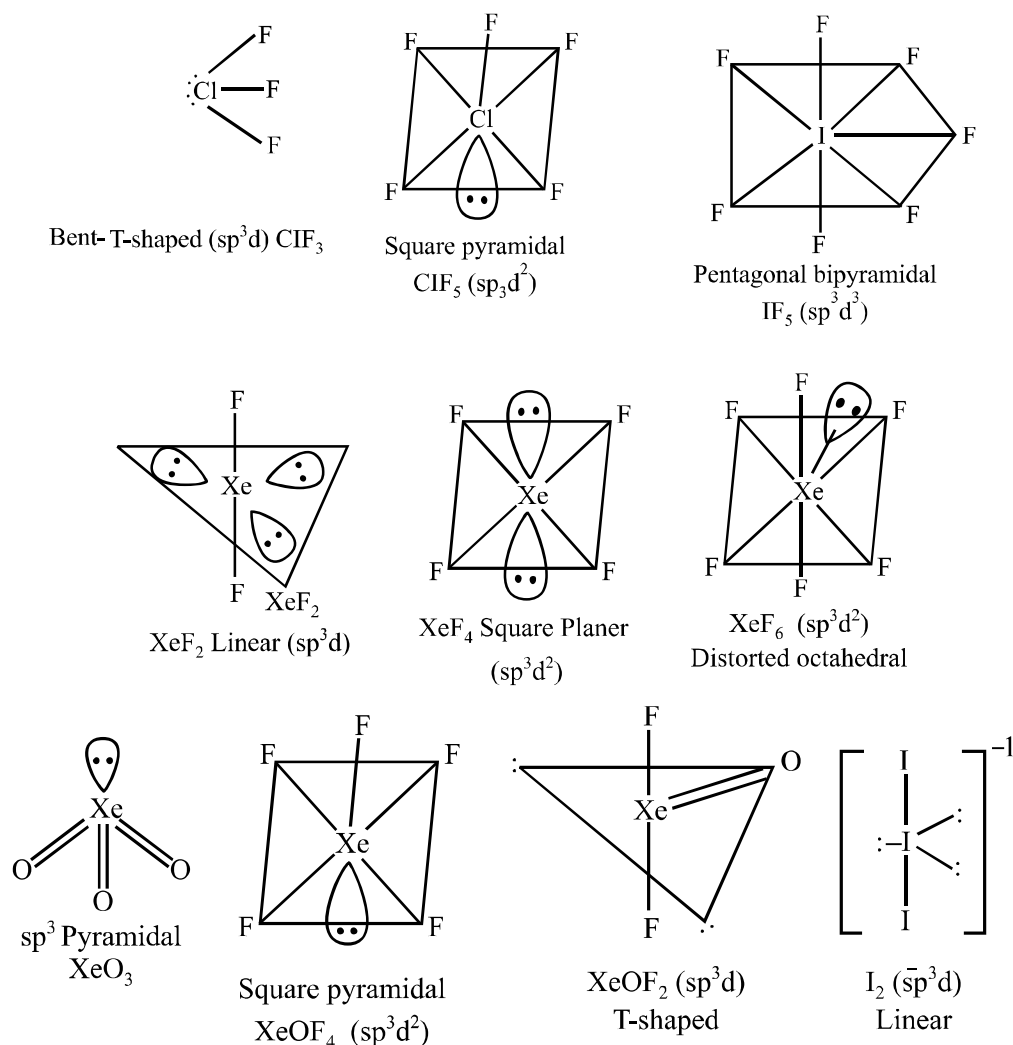




Oxy-acids of Nitrogen







VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 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.]

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

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

Q. 3. Maximum covalence of nitrogen is ‘4’ but the heavier elements of group 15 show covalence greater than ‘4’. Why ?

[Hint : Nitrogen is not having vacant d- orbitals in its octet, hence cannot expand its octet, while heavier members have vacant d-orbitals to expand their octet.]

- Q. 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-p multiple bonds are formed by N due to its small size.]

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

[Hint : Due to their stable electronic configuration (ns^2np^3).]

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

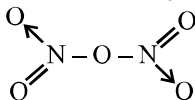
[Hint : NH_3 molecules are stabilized by intermolecular H-bonding, while PH_3 by weak van der Waals's forces.]

- Q. 7. NO_2 dimerises to form N_2O_4 . Why ?**

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

- Q. 8. Draw the structure of N_2O_5 molecule.**

Ans.



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

[Hint : Ag^+ (aq) + $2NH_3$ (aq) \rightarrow $[Ag(NH_3)_2]^+$ (aq)]

- Q. 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.]

- Q. 11. Write disproportionation reaction of H_3PO_3 ?**

[Hint : $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$]

- Q. 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. It can donate electron pair to central metal atom or ion.]

- Q. 13. Write the reaction of PCl_5 with heavy water.**

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

- Q. 14. What is laughing gas ? How is it prepared ?**

[Hint : N_2O , $NH_4NO_3 \rightarrow N_2O + 2H_2O$]

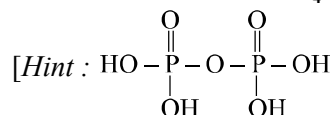
Q. 15. Why is white phosphorus kept under water ?

[Hint : Due to high angular strain, it is highly reactive and catches fire in air, hence kept under water.]

Q. 16. “Hydrophosphorus acid is a good reducing agent.” Justify with an example.

[Hint : $4\text{AgNO}_3 + \text{H}_3\text{PO}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Ag} + 4\text{HNO}_3 + \text{H}_3\text{PO}_4$]

Q. 17. Draw the structure of $\text{H}_4\text{P}_2\text{O}_7$ and find out its basicity.



As four $-\text{OH}$ groups are present, hence basicity is 4.]

Q. 18. Why is Bi (V) a stronger oxidant than Sb (V) ?

[Hint : Due to inert pair effect; + 3 oxidation state is more stable than + 5 oxidation state in Bi.]

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

[Hint : 3 bonds]

Q. 20. Give reason : In the solid state, PCl_5 behaves as an ionic species.

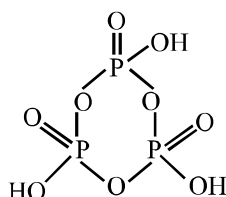
[Hint : It exists as an ionic solid $[\text{PCl}_4]^+[\text{PCl}_6]^-$]

Q. 21. Give reason : BiCl_3 is less covalent than PCl_3 .

[Hint : Due to more polarization power of P^{3+} ion than Bi^{3+} ion.]

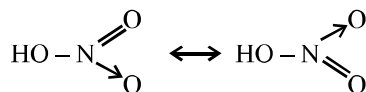
Q. 22. Draw the structure of $(\text{HPO}_3)_3$.

Hint :



Q. 23. In the structure of HNO_3 molecule, the N – O bond (121 pm) is shorter than N – OH bond (140 pm).

[Hint : Due to resonance N – O bond is having partial double bond character hence shorter than N – OH bond which is pure single bond character.]



Q. 24. Write the name and formula of neutral oxide of nitrogen.

[Hint : (i) Nitrous oxide/Dinitrogen oxide/Nitrogen (I) oxide N_2O .

(ii) Nitrogen monoxide/Nitrogen (II) oxide/Nitric oxide NO .]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)**Complete the following reactions :**

1. (i) $(\text{NH}_4)_2\text{G}_2\text{O}_7 \xrightarrow{\text{heat}}$
 (ii) $\text{NH}_4\text{Cl (aq)} + \text{NaNO}_2 \text{ (aq)} \rightarrow$
2. (i) $\text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow$
 (ii) $\text{FeCl}_3 \text{ (aq)} + \text{NH}_4\text{OH (aq)} \rightarrow$
3. (i) $\text{Ca}_3\text{P}_2 + \text{H}_2\text{O (l)} \rightarrow$
 (ii) $\text{I}_2 + \text{HNO}_3 \text{ (conc.)} \rightarrow$
4. (i) $\text{Ba(N}_3)_2 \xrightarrow{\text{heat}}$
 (ii) $4\text{H}_3\text{PO}_3 \xrightarrow{\text{heat}}$
5. (i) $\text{PH}_4\text{I} + \text{KOH} \rightarrow$
 (ii) $\text{HgCl}_2 + \text{PH}_3 \rightarrow$
6. (i) $\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow$
 (ii) $\text{PCl}_5 + \text{H}_2\text{O} \rightarrow$
7. (i) $\text{NO}_3^- + \text{Fe}^{2+} + \text{H}^+ \rightarrow$
 (ii) $\text{Zn} + \text{HNO}_3 \text{ (dil.)} \rightarrow$
8. (i) $\text{Zn} + \text{HNO}_3 \text{ (conc.)} \rightarrow$
 (ii) $\text{P}_4 + \text{HNO}_3 \text{ (conc.)} \rightarrow$
9. (i) $\text{NH}_3 + \text{O}_2 \xrightarrow[500\text{K, 9 bar}]{\text{Pt/Rh}}$
 (ii) $\text{P}_4 + \text{NaOH} + \text{H}_2\text{O} \rightarrow$
10. (i) $\text{NH}_3 \text{ (excess)} + \text{Cl}_2 \rightarrow$
 (ii) $\text{NH}_3 + \text{Cl}_2 \text{ (excess)} \rightarrow$
11. (i) $\text{P}_4 + \text{HNO}_3 \text{ (conc.)} \rightarrow$
 (ii) $\text{Cu} + \text{HNO}_3 \text{ (conc.)} \rightarrow$

Q. 12. Why is red phosphorus denser and less chemically reactive than white phosphorus ?

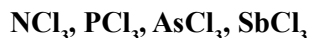
[Hint : Because it have polymeric structure consisting chains of P_4 tetrahedra, hence denser than white P while red P is not having angular strain as in white P, hence less reactive than white P.]

- Q. 13. (i) The acidic character of hydrides of group 15 increases from NH_3 to BiH_3 . Why ?**
- (ii) Phosphorus show marked tendency for catenation. Why ?**

[Hint : (i) Because from NH_3 to BiH_3 thermal stability decreases hence acidic character increases from NH_3 to BiH_3 .

(ii) Because phosphorus do not form $p\pi-p\pi$ multiple bond due to its bigger size.]

Q. 14. Arrange the following trichlorides in decreasing order of bond angle :



[Hint : $\text{NCl}_3 < \text{PCl}_3 < \text{AsCl}_3 < \text{SbCl}_3$]

Q. 15. How many P – O – P bonds are there in (i) $\text{H}_4\text{P}_2\text{O}_7$ (ii) P_4O_{10} ?

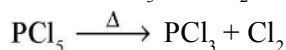
[Hint : (i) $\text{H}_4\text{P}_2\text{O}_7 = 01$ (ii) $\text{P}_4\text{O}_{10} = 05$]

Q. 16. At low temperature, NO_2 becomes colourless. Why ?

[Hint : NO_2 gets condensed to N_2O_4 .]

Q. 17. Give chemical reaction in support of the statement that all the bonds in PCl_5 molecule are not equivalent.

[Hint : PCl_5 dissociates into PCl_3 and Cl_2 on heating.]



Q. 18. (i) What is the covalency of N in N_2O_5 ?

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

[Hint : (i) 4

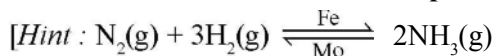
(ii) Because due to presence of vacant d-orbitals in the octet of 'p', it can expand its octet to form PCl_5 , while N cannot expand its octet.]

Q. 19. Arrange the following in the decreasing order of their basicity. Assign the reason :



[Hint : $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$]

Q. 20. Write the conditions that favour the formation of ammonia gas along with the reactions involved in Haber's process.

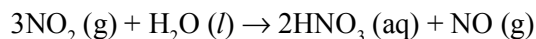
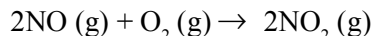
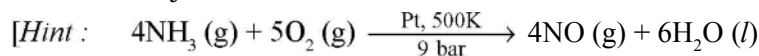


(i) High pressure (200 atm).

(ii) Moderate temperature (700 K).

(iii) Presence of catalyst Fe/FeO, with small amount of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.]

Q. 21. Explain the Ostwald's process to manufacture nitric acid. Give any two uses of HNO_3 .



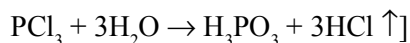
(68% by mass)

Uses : (i) Used in the manufacture of fertilizers, explosives.

(ii) Used as lab reagent.]

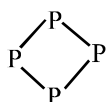
Q. 22. Why does PCl_3 fumes in moisture ? Give reaction also.

[Hint : PCl_3 hydrolyses in the presence of moisture giving fumes of HCl .

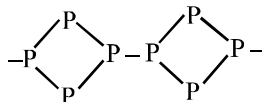


Q. 23. Draw the structure of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why ?

[Hint : White phosphorus exists as discrete P_4 tetrahedral molecule, while red phosphorus is polymeric consisting of chains of P_4 tetrahedra linked together.



White P



Red P

White P is more reactive than red P, due to angular strain in it.]

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. (i) How is HNO_3 prepared commercially ?

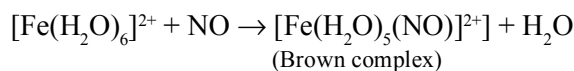
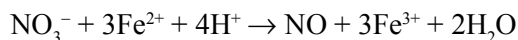
(ii) Write chemical equations of the reactions involved.

(iii) What concentration by mass of HNO_3 can be obtained ?

[Hint : Refer to Q. 21 SA-I type]

Q. 2. 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 : $\text{X} = \text{NO}_3^-$ salt,] [$\text{Y} = [\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$]



Q. 3. Explain each of the following :

- (i) The bond angles (O–N–O) are not of the same value in NO_2^- and NO_2^+ .
- (ii) BiH_3 is the strongest reducing agent amongst all the hydrides of group 15 elements.
- (iii) Ammonia has greater affinity for protons than phosphine.

[Hint : (i) Due to presence of lone pair of electron on N in NO_2^- .

- (ii) Bi–H bond dissociation enthalpy is least and releases hydrogen most easily.
- (iii) NH_3 is stronger Lewis base than PH_3 .]

Q. 4. Write balanced equation for the following reactions :

- (i) Zn is treated with dilute HNO_3 .
- (ii) Copper metal with conc. HNO_3 .
- (iii) Iodine is treated with conc. HNO_3 .

[Hint : (i) $4\text{Zn} + 10\text{HNO}_3 (\text{dil.}) \rightarrow 4\text{Zn}(\text{NO}_3)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O}$

(ii) $3\text{Cu} + 8\text{HNO}_3 (\text{dil.}) \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$

(iii) $\text{I}_2 + 10\text{HNO}_3 (\text{conc.}) \rightarrow 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$]

Q. 5. A translucent white 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. (A) with excess of chlorine forms (D) which hydrolyses to form compound (E). Identify the compounds (A) to (E).

[Hint : A : White phosphorus, B : Red phosphorus, C : PH_3 , D : PCl_5 , E : H_3PO_4]

Q. 6. Assign the appropriate reason for the following :

- (i) Nitrogen exists as diatomic molecule and phosphorus as P_4 at room temperature. Why ?
- (ii) Why does $\text{R}_3\text{P}=\text{O}$ exist but $\text{R}_3\text{N}=\text{O}$ does not ? (R = an alkyl group).
- (iii) Why is N_2 unreactive at room temperature ?

[Hint : (i) Due to its small size and high electronegativity, N forms $p\pi - p\pi$ multiple bond ($\text{N} \equiv \text{N}$) whereas P does not form $p\pi - p\pi$ bonds but forms P – P single bond.

- (ii) In $\text{R}_3\text{N}=\text{O}$, N should have a covalence of 5 so the compound $\text{R}_3\text{N}=\text{O}$ does not exist since maximum covalence shown by N cannot exceed 4.]

GROUP 16 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Explain why SF_4 is easily hydrolysed, whereas SF_6 is resistant to hydrolysis ?

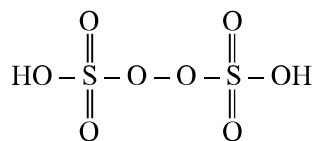
[Hint : Water molecule cannot attack 'S' atom due to steric hinderance and 'S' atom is also coordinately saturated in SF_6 molecule.]

Q. 2. 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.]

Q. 3. Draw the structure of $\text{H}_2\text{S}_2\text{O}_8$ and find the number of S – S bond, if any.

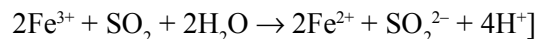
[Hint :



Number of S – S bond \Rightarrow 0.]

Q. 4. What happens when sulphur dioxide gas is passed through an aqueous solution of a Fe(III) salt ?

[Hint : It converts Fe^{3+} ions to Fe^{2+} ions.

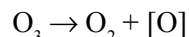


Q. 5. All the bonds in SF_4 are not equivalent. Why ?

[Hint : It is having see-saw shape. (4BP + 1LP)]

Q. 6. O_3 acts as a powerful oxidizing agent. Why ?

[Hint : Due to the ease with which it liberates atoms of nascent oxygen.]



Q. 7. Which one of the following is not oxidized 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.]

Q. 8. Why does oxygen not show an oxidation state of + 4 and + 6 ?

[Hint : Due to absence of vacant d-orbitals in the octet of oxygen.]

Q. 9. Oxygen and sulphur in vapour phases are paramagnetic in nature. Explain why ?

[Hint : Due to presence of unpaired electrons in anti-bonding molecular orbitals in them.]

Q. 10. Thermal stability of hydrides of group 16 elements decreases down the group. Why ?

[Hint : Because down the group E – H bond dissociation enthalpy decreases.]

Q. 11. Why are the two S – O bonds in SO_2 molecule have equal strength ?

[Hint : Due to resonance, two S – O bonds have partial double bond character, hence have equal strength.]

Q. 12. $K_{a2} \ll K_{a1}$ for H_2SO_4 in water, why ?

[Hint : $\text{H}_2\text{SO}_4 (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_3\text{O}^+ (\text{aq}) + \text{HSO}_4^- (\text{aq}); K_{a1} > 10$

$\text{HSO}_4^- (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_3\text{O}^+ (\text{aq}) + \text{SO}_4^{2-} (\text{aq}); K_{a2} = 10^{-2}$

K_{a2} is less than K_{a1} because HSO_4^- ion has much less tendency to donate a proton.]

Q. 13. H_2O is a liquid while inspite of a higher molecular mass, H_2S is a gas. Explain.

[Hint : H_2O molecules are stabilized by intermolecular hydrogen bonding, while H_2S by weak van der Waal's forces.]

Q. 14. The electron gain enthalpy with negative sign for oxygen (-141 KJ mol^{-1}) is numerically less than that for sulphur (-200 KJ mol^{-1}). Give reason.

[Hint : Due to smaller size of oxygen than sulphur electron-electron repulsion is more in oxygen than sulphur.]

Q. 15. Dioxygen O_2 is a gas while sulphur (S_8) is a solid. Why ?

[Hint : Because oxygen is smaller in size hence have capacity to form $p\pi-p\pi$ multiple bond, exists as dioxygen (O_2), whereas due to bigger size sulphur do not form multiple bond and exist as S_8 .]

Q. 16. In the preparation of H_2SO_4 by contact process, why is SO_3 not absorbed directly in water to form H_2SO_4 ?

[Hint : Because it forms a dense fog of sulphuric acid which does not condense easily.]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Write the chemical equations of the following reactions :

(a) Glucose is heated with conc. H_2SO_4 .

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

[Hint : (a)

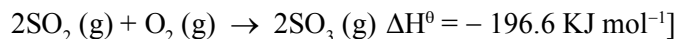
(b) $\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HNO}_3$]

Q. 2. Mention the favourable conditions for the manufacture of sulphuric acid by contact process.

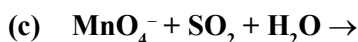
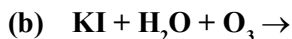
[Hint : (i) Low temperature (operating temperature is 720 K).

(ii) High pressure (2 bar).

(iii) Presence of catalyst (V_2O_5).



Q. 3. Complete the following reactions :



Q. 4. Explain why :

(a) H_2S is more acidic than H_2O .

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

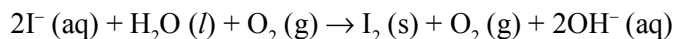
(c) SF_6 is inert and stable but SF_4 is reactive.

(d) Sulphur has greater tendency for catenation than oxygen.

[Hint : (iii) Because six F atoms protect the sulphur atom from attack by any reagent due to steric hindrance but four F atoms in SF_4 cannot offer much steric hindrance, hence reactive.]

Q. 5. How is O_3 estimated quantitatively ?

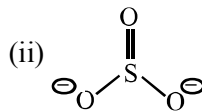
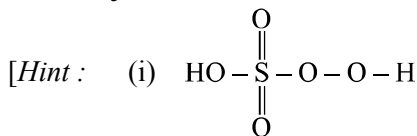
[Hint : O_3 reacts with an excess of KI solution buffered with a borate buffer, I_2 is liberated which is titrated against standard solution of sodium thiosulphate.]



Q. 6. Explain why O_3 is thermodynamically less stable than O_2 ?

[Hint : Because O_3 is endothermic compound/decomposition of O_3 is exothermic and ΔG is negative/decomposition of O_3 is spontaneous.]

Q. 7. Draw the structure of :



SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

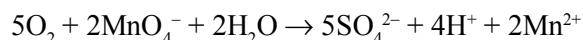
Q. 1. (i) How does O_3 react with lead sulphide ? Write chemical equation.

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

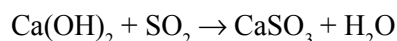
(iii) SO_2 behaves with lime water similar to CO_2 . Explain why ?

[Hint : (i) $PbS (s) + 4O_3 (g) \rightarrow PbSO_4 (s) + 4O_2 (g)$

(ii) It decolourises acidified $KMnO_4$ solution.



(iii) It turns lime water milky due to the formation of insoluble $CaSO_3$.



(milky)

Q. 2. Complete the reactions :

(i) $CaF_2 + H_2SO_4 (conc.) \rightarrow$

(ii) $C_{12}H_{22}O_{11} + H_2SO_4 (conc.) \rightarrow$

(iii) $SO_2 + MnO_4^- + H_2O \rightarrow$

Q. 3. 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 aq. $KMnO_4$ solution. Identify the solid 'A' and the gas 'B' and write the reaction involved.

[Hint : A = S_8 ; B = $SO_2 (g)$]

(i) How is SO_2 prepared in laboratory ?

(ii) What happens when SO_2 is passed through water and reacts with $NaOH$? Write balanced equation.

(iii) Write its any two uses.

Hint : (i) $Na_2SO_3 (s) + H_2SO_4 (aq) \rightarrow SO_2 (g) + Na_2SO_4 (aq) + H_2O (l)$

(ii) $2NaOH + SO_2 (g) \rightarrow Na_2SO_3 (aq) + H_2O$



(iii) It is used as bleaching agent and disinfectant.

Q. 4. Assign reason for the following :

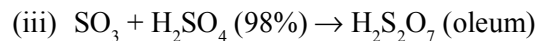
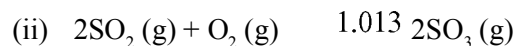
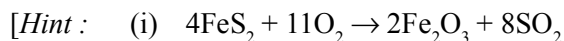
(i) Sulphur in vapour state exhibits paramagnetism.

(ii) H_2O is less acidic than H_2Te .

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

[Hint : (iii) Due to bigger size of Cl.]

Q. 5. Write contact process for the manufacture of king of chemicals.



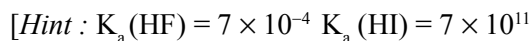
GROUP 17 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Explain why fluorine forms only one oxoacid, HOF.

[Hint : Because of unavailability of d-orbitals in its valence shell.]

Q. 2. Why HF is the weakest acid and HI is the strongest ?

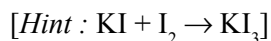


Intermolecular H-bonds in H – F and high bond dissociation enthalpy of H – F makes it weakest and weak bond in H – I makes it strongest.]

Q. 3. Explain why halogens are strong oxidizing agents.

[Hint : High electronegativity and more negative electron gain enthalpies of halogens.]

Q. 4. I_2 is more soluble in KI than in water. Why ?



Q. 5. What is cause of bleaching action of chlorine water ? Explain it with chemical equation.

[Hint : Formation of nascent oxygen.]

Q. 6. Electron gain enthalpy of fluorine (F) is less negative than that of chlorine (Cl). Why ?

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

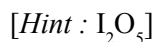
Q. 7. Why can't we prepare HBr by heating KBr with sulphuric acid ?

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

Q. 8. Explain why : ICl is more reactive than I_2 ?

[Hint : Because I – Cl bond is weaker than I – I bond.]

Q. 9. Which oxide of iodine is used for the estimation of carbon mono oxide ?



Q. 10. Arrange the following oxoacids of chlorine in increasing order of acid strength :



[Hint : $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$]

Q. 11. Why does fluorine not play the role of a central atom in interhalogen compounds ?

[Hint : Due to smallest size of F.]

Q. 12. Fluorine exhibit only – 1 oxidation state whereas other halogens exhibit +ve oxidation states also. Explain why ?

[Hint : Due to absence of vacant d-orbitals in the octet of F.]

Q. 13. ClF_3 exists but FCl_3 does not. Why ?

[Hint : Because F does not show oxidation state other than – 1.]

Q. 14. Despite lower value of its electron enthalpy with negative sign, fluorine is a stronger oxidizing agent than chlorine. Explain.

[Hint : Due to its low bond dissociation enthalpy (F–F bond) and high hydration enthalpy of F^- .]

Q. 15. ClF_3 molecule has a bent T-shaped structure and not a trigonal planar structure. Explain.

[Hint : Due to presence of 2LP and 3BP.]

Q. 16. What happens when NaCl is heated with H_2SO_4 in the presence of MnO_2 ?

[Hint : $4\text{NaCl} + \text{MnO}_2 + 4\text{H}_2\text{SO}_4 \rightarrow \text{MnCl}_2 + 4\text{NaHSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$]

Q. 17. With what neutral molecule ClO^- is isoelectronic ?

[Hint : ClF or OF_2 .]

Q. 18. Why HF acid is stored in wax coated glass bottle ?

[Hint : HF is corrosive, hence HF attacks glass surface.]

Q. 19. Bond dissociation enthalpy of F_2 is less than that of Cl_2 . Explain why ?

[Hint : F_2 is having higher electron-electron repulsion due to its smaller size, as compared to Cl_2 .]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. (i) Interhalogen compounds are more reactive than halogens except F_2 . Why ?

(ii) Give one important use of ClF_3 .

[Hint : (i) Because X – X bond in interhalogens is weaker than X – X bond in halogens except F – F bond.

(ii) ClF_3 is used for the production of UF_6 .]

Q. 2. (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.

[Hint : (i) $\text{Ca}(\text{OCl})_2 \cdot \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$]

Q. 3. A colourless pungent smelling gas, which easily liquefies 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 : $\text{NaCl} + \text{H}_2\text{SO}_4 (\text{conc.}) \rightarrow \text{NaHSO}_4 + \text{HCl}$]

Q. 4. NO_2 readily dimerise, whereas ClO_2 does not. Why ?

[Hint : Due to bigger size of Cl than N.]

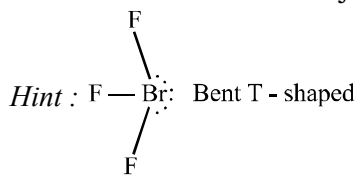
Q. 5. Compare the oxidizing powers of F_2 and Cl_2 on the basis of bond dissociation enthalpy, electron gain enthalpy of halogens and hydration enthalpy of halide ions.

[Hint : It is due to low enthalpy of dissociation of F – F bond and high hydration enthalpy of F^- .]

Q. 6. Which fluorinating agent are oftenly used instead of F_2 ? Write chemical equation showing their use as fluorinating agents.

[Hint : $\text{U} (\text{s}) + 3\text{ClF}_3 (\text{l}) \rightarrow \text{UF}_6 (\text{g}) + 3\text{ClF} (\text{g})$]

Q. 7. Draw the structure of BrF_3 .



Complete the following reactions :

8. (i) $\text{Al}_2\text{O}_3 (\text{s}) + \text{NaOH} (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightarrow$

(ii) $\text{HCl} + \text{O}_2 \rightarrow$

9. (i) $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \rightarrow$

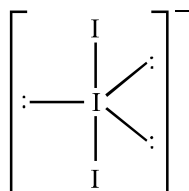
(ii) $\text{N}_2 (\text{excess}) + \text{Cl}_2 \rightarrow$

10. (i) $\text{Na}_2\text{SO}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow$

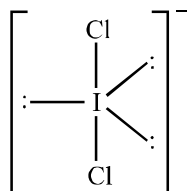
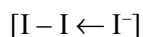
(ii) $\text{N}_2 + \text{Cl}_2 (\text{excess}) \rightarrow$

11. (i) $\text{Cl}_2 + \text{NaOH}$ (cold & dil.) \rightarrow
 (ii) $\text{Cl}_2 + \text{NaOH}$ (hot & conc.) \rightarrow
12. (i) $\text{Fe} + \text{HCl} \rightarrow$
 (ii) $\text{Cl}_2 + \text{F}_2$ (excess) \rightarrow
13. (i) $\text{U} + \text{ClF}_3 \rightarrow$
 (ii) $\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{Cl}_2 \rightarrow$
- Q. 14. Draw the structure of : (a) I_3^- (b) ICl_2^- .**

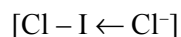
Hint :



Linear



Linear



SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. 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 are more polarized than the smaller ions by a particular cation.

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

- (iii) $2\text{KI} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{I}_2$



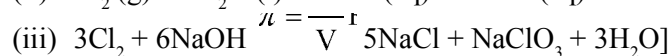
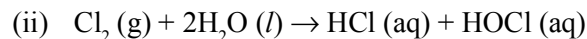
(colourless)

Q. 2. 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.

- (i) Identify X_2 , name the group to which it belongs.
 (ii) What are the products obtained when X_2 reacts with H_2O ? Write chemical equation.

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

[Hint : (i) Cl_2 , 17 group.



Q. 3. Arrange the following in the order of the property indicated for each set :

(i) F_2, Cl_2, Br_2, I_2 (Increasing bond dissociation energy)

(ii) HF, HCl, HBr, HI (decreasing acid strength)

(iii) $NH_3, PH_3, AsH_3, SbH_3, BiH_3$ (Decreasing base strength)

[Hint : (i) 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. Stronger electron-electron repulsions among the lone pairs in F_2 molecule make its bond dissociation enthalpy exceptionally low.

(ii) Acid strength depends upon H – X bond dissociation enthalpy. As the size of 'X' atom increases, bond dissociation enthalpy of H – X decreases.

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

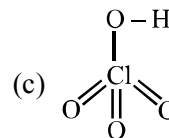
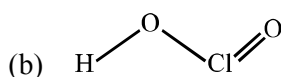
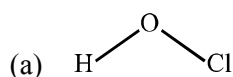
Q. 4. Draw the structure of :

(i) Hypochlorous acid

(ii) Chlorous acid

(iii) Perchloric acid

Hint :



Q. 5. Which is more acidic among $HClO_4$ and HIO_4 ? Why ?

[Hint : $HClO_4$ is more acidic than HIO_4 . Because Cl is more electronegative than Br, due to which ClO_3 group have more tendency to withdraw electrons of O – H bond towards itself as compared to BrO_3 group.]

GROUP 18 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What inspired N. Barlett for carrying out reaction between Xe and PtF_6 ?

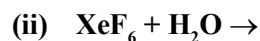
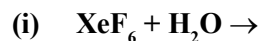
[Hint : Almost same ionization enthalpy of oxygen and Xe.]

- Q. 2. Predict the shape and the asked angle (90° or more or less) in the following case :**
 XeF_2 and the angle $\text{F} - \text{Xe} - \text{F}$
 [Hint : Linear, 180°]
- Q. 3. Structure of Xenon fluoride cannot be explained by valence bond approach. Why ?**
 [Hint : Due to fully filled octet of Xe.]
- Q. 4. Why do some noble gases form compounds with fluorine and oxygen only ?**
 [Hint : Due to high electronegativity of F and oxygen.]
- Q. 5. XeF_2 has a straight linear structure and not a bent angular structure. Why ?**
 [Hint : In XeF_2 , 2 bond pairs and 3 lone pairs are present hence linear structure.]
- Q. 6. Why do noble gases have very low boiling point ?**
 [Hint : Because noble gases are stabilized by weak van der Waal's forces.]
- Q. 7. Write the chemical equation involved in the preparation of XeF_4 .**
 [Hint : $\text{Xe (g)} + 2\text{F}_2 \text{ (g)} \rightarrow \text{XeF}_4 \text{ (s)}$]
 Ratio 1 : 5
- Q. 8. Write IUPAC name of $\text{O}_2^+[\text{PtF}_6]$.**
 [Hint : Dioxygenyl hexafluoroplatinate(iv).]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

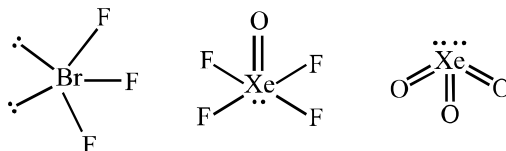
- Q. 1. Suggest reason why only known binary compounds of noble gases are fluorides and oxides of Xenon and to a lesser extent of Krypton.**
 [Hint : F and O are most electronegative elements Kr and Xe both have low ionization enthalpies as compared to He and Ne.]
- Q. 2. (i) Hydrolysis of XeF_6 is not regarded as a redox reaction. Why ?**
(ii) Write a chemical equation to represent the oxidizing nature of XeF_4 .
 [Hint : (i) Because oxidation number of Xe does not change during hydrolysis of XeF_6 .
 (ii) $\text{XeF}_4 + 2\text{H}_2 \rightarrow \text{Xe} + 4\text{HF}$]
- Q. 3. Write chemical equations when :**
(i) XeF_2 is hydrolysed.
(ii) PtF_6 and Xenon are mixed together.
 [Hint : (i) $2\text{XeF}_2 \text{ (s)} + 2\text{H}_2\text{O (l)} \rightarrow 2\text{Xe (g)} + 4\text{HF (aq)} + \text{O}_2 \text{ (g)}$
 (ii) $\text{Xe} + \text{PtF}_6 \rightarrow \text{Xe}^+[\text{PtF}_6]^-$]

Q. 4. Complete the reactions :



Q. 5. Draw the structure of BrF_3 , XeOF_4 , XeO_3 using VSEPR theory.

[Hint :



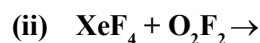
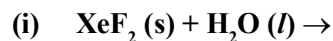
Q. 6. Account for the following :

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

(ii) The majority of known noble gas compounds are those of Xenon. Why ?

[Hint : (ii) Xe has low ionization enthalpy as compared to other noble gases.]

Q. 7. Write the chemical reactions :



SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Assign reason to the following :

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

(ii) Helium is used by scuba divers.

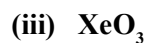
(iii) No chemical compound of helium is known.

[Hint : (i) Due to their electron configuration.

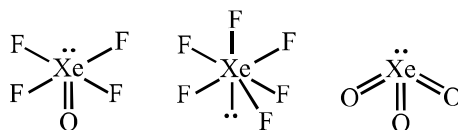
(ii) Due to its less solubility in blood.

(iii) Due to its high ionization enthalpy.]

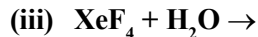
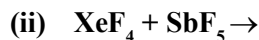
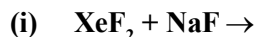
Q. 2. Draw the structure of :



[Hint :

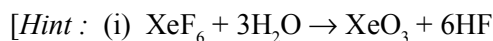


Q. 3. Complete the reactions :

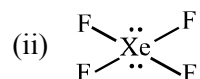
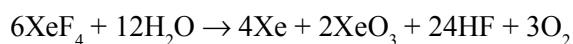


Q. 4. (i) How is XeO_3 prepared from XeF_6 ? Write the chemical equation for the reaction.

(ii) Draw the structure of XeF_4 .



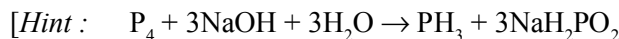
Or



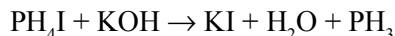
LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 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 adsorption in CuSO_4 ? How can you prove that PH_3 is basic in nature ?

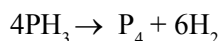
Write chemical equations for all the reactions involved.



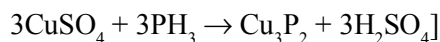
It is purified by absorbing it in HI to form PH_4I which on treating with KOH gives off phosphine.



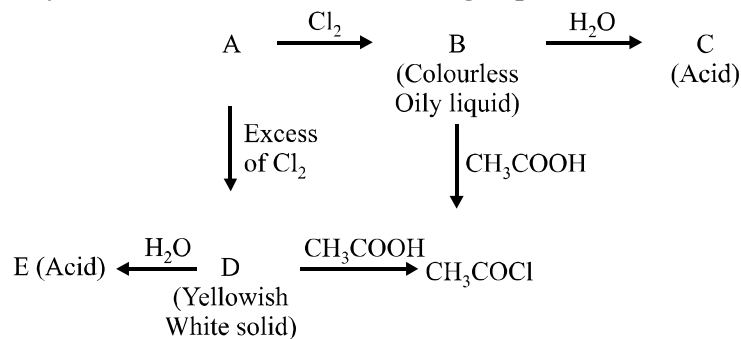
PH_3 in water decomposes into red phosphorus and hydrogen in presence of light.



Reaction with CuSO_4 :

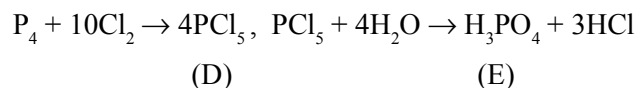
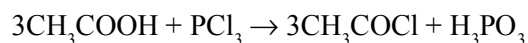
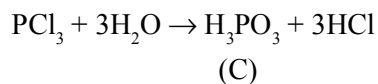


Q. 2. Identify A, B, C, D and E in the following sequence of reactions :

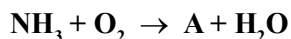


Complete the reactions of the above mentioned sequence.

[Hint : A is P_4 , B is PCl_3 .

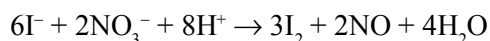
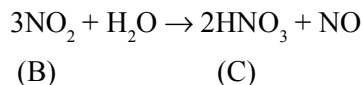
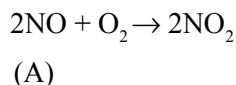


Q. 3. Write the structure of A, B, C, D and E in the following sequence of reactions :



Complete the 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 .



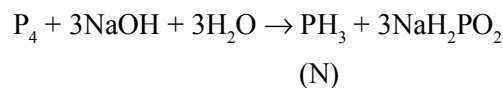
Q. 4. A waxy translucent solid, M, insoluble in water but soluble in CS_2 glows in dark. M dissolves in NaOH in an inert atmosphere giving a poisonous gas (N). Also M catches fire to give dense white fumes of Q.

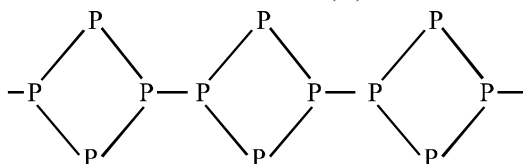
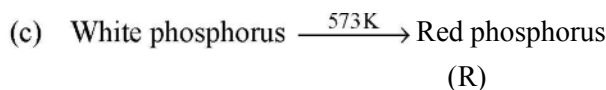
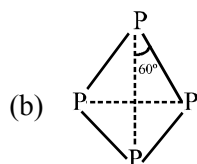
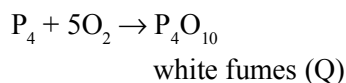
(a) Identify M, N and Q and write the chemical equations of the reactions involved.

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

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

[Hint : (a) M is white phosphorus.





Q. 5. Assign a possible reason for the following :

- Stability of + 5 oxidation state decreased and that of + 3 oxidation state increases down the group 15 elements.
- H_2O is less acidic than H_2S .
- SF_6 is inert while SF_4 is highly reactive towards hydrolysis.
- H_3PO_2 and H_3PO_3 act as reducing agents while H_3PO_4 does not.
- Helium gas is used by scuba divers.

[Hint : (a) Due to inert pair effect.

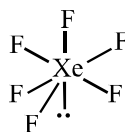
- Due to more bond dissociation enthalpy of O – H as compared to S – H bond.
- Due to more steric hindrance offered by six F in SF_6 as compared to SF_4 .
- Due to presence of P – H bond in them.
- He is very less soluble in blood.]

Q. 6. (a) How is XeF_6 prepared from the XeF_4 ? Write the chemical equation for the reaction.

- Deduce the structure of XeF_6 using VSEPR theory.
- How does XeF_2 reacts with PF_5 ?
- Give one use each of helium and neon.
- Write the chemical equation for the hydrolysis of XeF_4 .

[Hint : (a) $\text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2$

- Distorted octahedral (6BP + 1LP)



- (c) $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+[\text{PF}_6]^-$
- (d) He is used in filling balloons/used by scuba divers.
Ne is used in discharge tubes, advertisement display purposes.
- (e) $6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2$

MATCHING TYPE QUESTIONS

Q. 1. 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

Q. 2. Match the formula 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

Q. 3. 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

Q. 4. 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

Q. 5. 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

ANSWERS

- | | | | |
|--------------|-----------|-----------|-----------|
| 1. (A) – (1) | (B) – (3) | (C) – (4) | (D) – (2) |
| 2. (A) – (4) | (B) – (1) | (C) – (2) | (D) – (3) |
| 3. (A) – (4) | (B) – (3) | (C) – (1) | (D) – (2) |
| 4. (A) – (3) | (B) – (2) | (C) – (1) | (D) – (4) |
| 5. (A) – (2) | (B) – (3) | (C) – (2) | (D) – (4) |

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Chlorofluorocarbons (CFCs) and gas emitted from the exhaust system of supersonic aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

- Name the gas emitted from the exhaust of supersonic aeroplanes.
- Name the element of CFCs which depletes ozone.
- Write the chemical reactions involved in the ozone layer depletion.
- Mention the values that are learnt by the students in the depletion of ozone layer.

- Q. 2.** A student accidentally spills concentrated H_2SO_4 on his hand. Before the teacher gets to know, his friend washed his hands with water and also with soap but the burning sensation on hand was still going on. The friend then rubs the paste of sodium bicarbonate on his hand and then washed with water, finally the burning sensation is relieved.
- (i) Mention the values shown by student's friend.
 - (ii) Can you recommend another substance available in the laboratory which can be used instead of sodium bicarbonate ?
 - (iii) Write the chemical reaction involved in the treatment of acid burn with sodium bicarbonate.
 - (iv) Can we use NaOH solution in place of NaHCO_3 ? If not, why ?
- Q. 3.** Ramu, a caretaker of swimming pool was using chlorine for disinfecting swimming pool water. His friend Jagat, also a swimming pool caretaker, was using ozone in place of chlorine.
- (i) How do chlorine and ozone disinfect water ?
 - (ii) In your opinion, which is better way of disinfecting water in a swimming pool ?
 - (iii) Mention the values associated with your reply.