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 ?

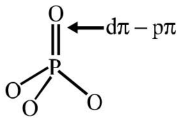
   (iii) Though nitrogen forms pentoxide but it does not form pentachloride. Why ?

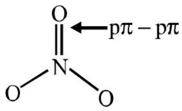
   (iv) Fluorine forms only one oxoacid while other halogens form a number of oxoacids. Why ?

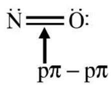
2. The first member of p-block elements displays greater ability to form pπ-pπ bond(s) with itself, (*e.g.,* C=C, C≡C, N=N, N≡N) and with the other elements of second period, for example, C=O, C≡N, N=O compared to the subsequent members of the group.

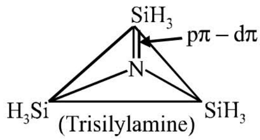
   This is because p-orbitals of the heavier members are so large and diffuse that they cannot have effective sideways overlapping. Heavier members can form p π-dπ bonds with oxygen.

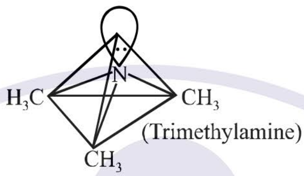
   Nitrogen rarely forms pπ-dπ bonds with heavier elements as in case of trisilylamine $(SiH_3)_3N$.











Now, the following questions can be explained using the above 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.]

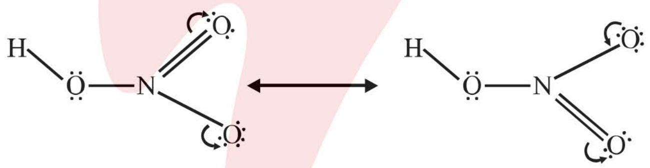
(vi) $AsCl_5$ is less stable than $SbCl_5$.

[*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.

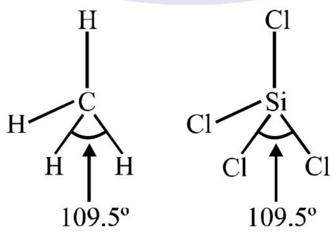


Now the following questions can be explained on the basis of this concept :

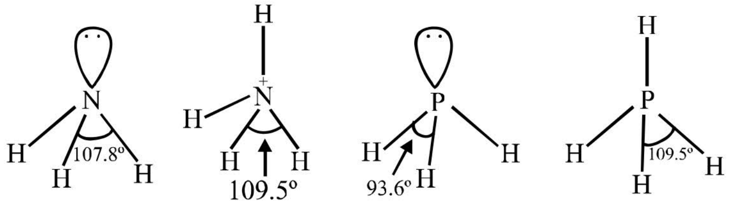
(i) In SO_2, the two sulphur-oxygen bonds are identical. Explain why ?

(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 tom, 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 Ip-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 :

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

(ii) 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 :

$PH_3 < AsH_3 < SbH_3 < NH_3$	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

(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.

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. $(SiH_3)_3N$ 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 $d\pi$-$p\pi$ 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.

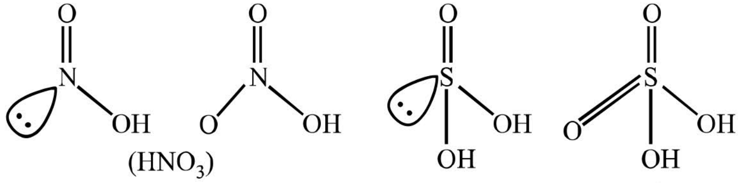
Explain why :

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

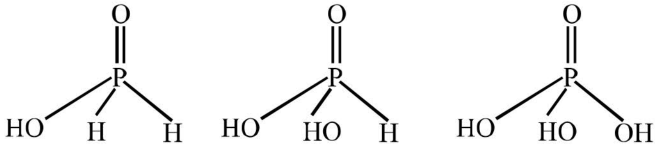
(ii) $SbCl_5$ is more covalent than $SbCl_3$.

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

Oxoacids of N, P and halogens :

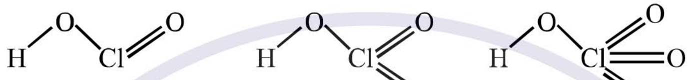


Stronger than HNO_3 H_2SO_3 Stronger than H_2SO_3



(Monophonic) (H_3PO_2) (Diprotic) (H_3PO_3) (Triprotic) (H_3PO_4)

(HOF) (HClO)



($HClO_3$) ($HClO_4$) ($HClO_4$)

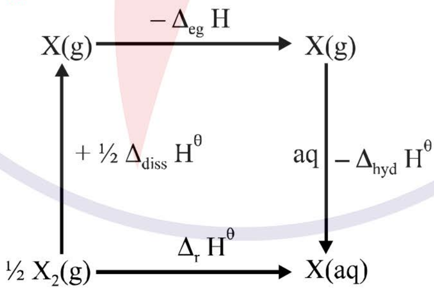
Strength of Oxo Acids

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 $\Delta_r H^\theta = \frac{1}{2}\Delta_{diss}H^\theta - \Delta_{eg}H^\theta - \Delta_{hyd}H^\theta$ the higher will be oxidizing 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, like $\Delta_{diss}H^\theta$, $\Delta_{eg}H^\theta$ and $\Delta_{hyd}H^\theta$.

(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

1. $(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$
2. $FeCl_3\ (aq) + NH_4OH\ (aq) \rightarrow Fe_2O_3.xH_2O\ (s) + NH_4Cl\ (aq)$
3. $Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$
4. $AgCl\ (s) + 2NH_3\ (aq) \rightarrow [Ag(NH_3)_2]Cl$
5. $2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 4PbO + O_2$
6. $4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$
7. $3Cu + 8HNO_3\ (dil.) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
8. $Cu + 4HNO_3\ (conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
9. $4Zn + 10HNO_3\ (dil.) \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$
10. $Zn + 4HNO_3\ (conc.) \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$
11. $I_2 + 10HNO_3\ (conc.) \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$
12. $S_8 + 48HNO_3\ (conc.) \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$
13. $P_4 + 20HNO_3\ (conc.) \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$
14. Chemistry of ring test :

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

    $[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$
15. $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$
16. $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$
17. $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$
18. $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
19. $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 3HCl$
20. $4H_3PO_3 \xrightarrow{heat} 3H_3PO_4 + PH_3$
21. $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$
22. $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
23. $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$
24. $2F_2\ (g) + 2H_2O\ (l) \rightarrow 4H^+\ (aq) + 4F^-\ (aq) + O_2\ (g)$
25. $X_2\ (g) + H_2O\ (l) \rightarrow HX\ (aq) + HXO\ (aq)\ (X = Cl, Br)$
26. $4I^-\ (aq) + 4H^+\ (aq) + O_2 \rightarrow 2I_2\ (s) + 2H_2O\ (l)$

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

28. $2NaOH\ (dil) + X_2 \xrightarrow{Cold} NaX + NaOX + H_2O$

29. $6NaOH\ (conc) + 3X_2 \xrightarrow{heat} 5NaX + NaXO_3 + 3H_2O$ $(X_2 = Cl_2, Br_2, I_2)$

30. $2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

31. $NaCl + H_2SO_4 \xrightarrow{heat} NaHSO_4 + HCl$

32. $XeF_2 + PF_5 \rightarrow [XeF]^+[PF_6]^-$

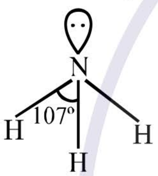
33. $XeF_6 + MF \rightarrow M^+[XeF_7]^-$ (M = Na, K, Rb or Cs)

34. $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

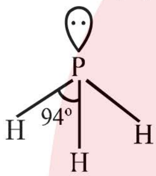
35. $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

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

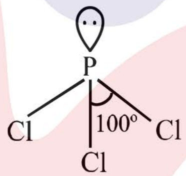
37. $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$



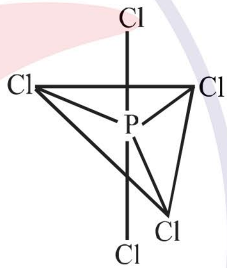
NH_3
Sp_3 (Pyramidal)



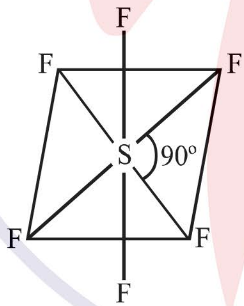
PH_3
Sp^3 (Pyramidal)



Sp^3 (Pyramidal)
PCl_3

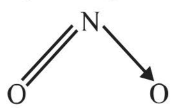


Sp^3d (Trigonalbiphyramidal)



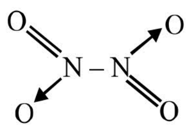
SF_6
Sp^3d (octahedral)

Oxides of Nitrogen
:N = 0
Nitric oxide (colourless)
paramagnetic

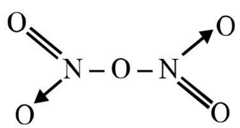


Sp^2 (NO_2) Bentmolecule
(brown) Paramagnetic

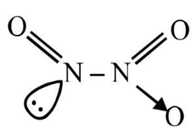
$N \equiv N \rightarrow O$
(N_2O) Colourless
Linear



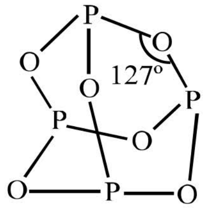
N_2O_4 (Colourless)
(diamagnetic)



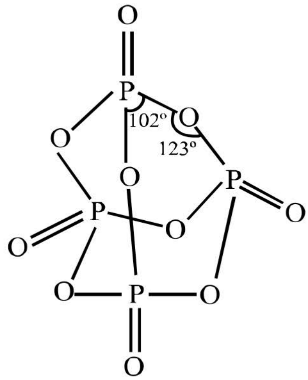
N_2O_5 (Colourless)
(diamagnetic)



(N_2O_3)
Pale blue solid

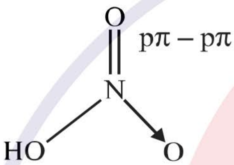


dimer P_2O_3

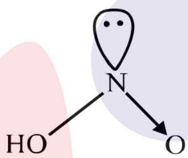


dimer of P_2O_5

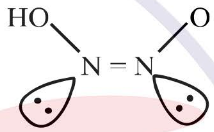
Oxy-acids of Nitrogen



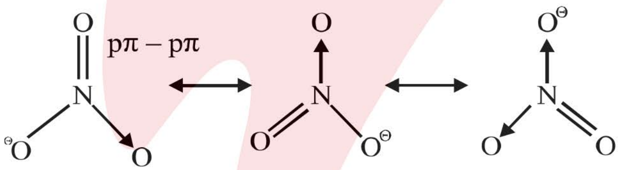
(HNO_3)
Colourless



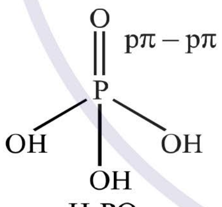
(HNO_3)
Para blue



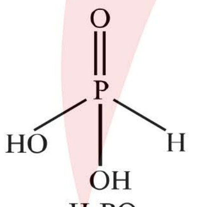
Hyponitrous acid



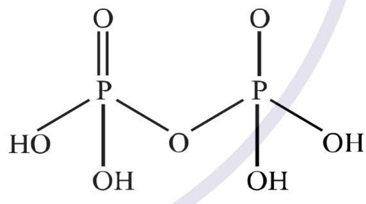
Resonating structure of NO_3^-



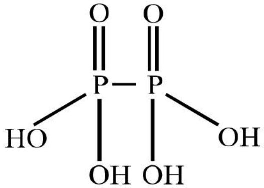
H_3PO_4
(Phosphoric acid)
tribasic



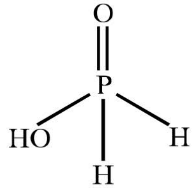
H_3PO_3
Phosphoric acid
(Dibasic)



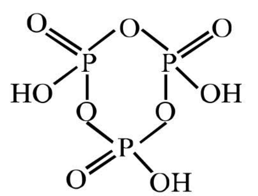
$H_4P_2O_7$
Pyrophosphoric acid
(tetrabasic)



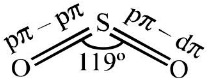
Hypophosphoric acid
$H_4P_2O_6$ (tetrabasic)



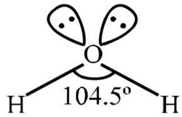
H_3PO_2
(Hypophosphoric acid)
(Monobasic)



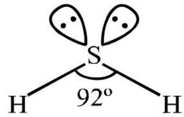
Cyclic meta phosphoric
acid $(HPO_3)_n$



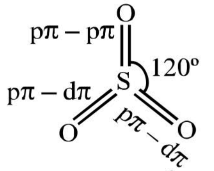
sp^3
Bent molecules



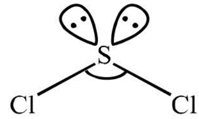
H_2O (sp^3)
V-shape

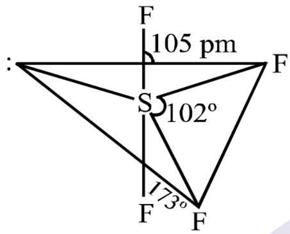


H_2O (sp^3)
V-shape

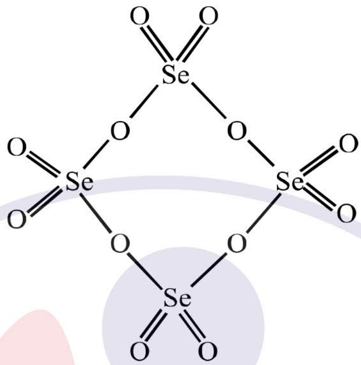


Planer Sp^2

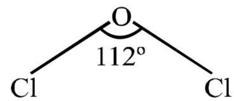




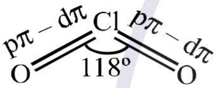
SF_4
Trigonal pyramidal sp3d
Oxy-acids of sulphur



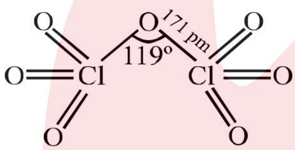
Cyclic tetramer of SeO_2



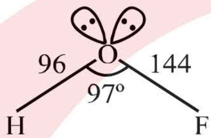
Cl_2O



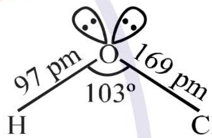
ClO_2

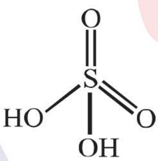


Cl_2O_7

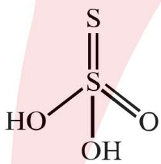


Cl_2O

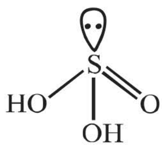




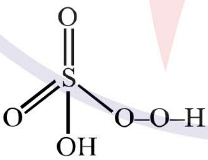
(H_2SO_4)
Sulphuric acid



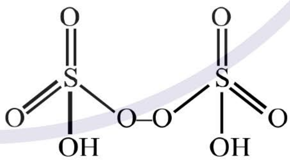
($H_2S_2O_3$)
(Thiosulphuric acid)



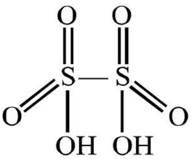
(H_2SO_3)
(Sulphurous acid)



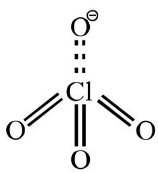
Peroxomonosulphuric acid
(Caro's acid)



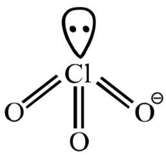
Peroxodisulphuric acid
($H_2S_2O_3$) Marshall's acid



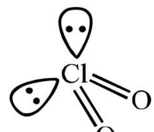
Dithionic acid ($H_2S_2O_5$)



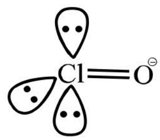
ClO_4^-



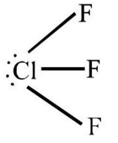
ClO_3^-



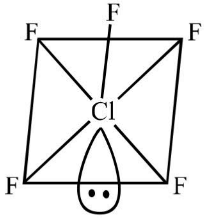
ClO_2^-



ClO^-

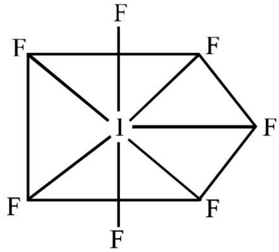


Bent- T-shaped (sp^3d) ClF_3



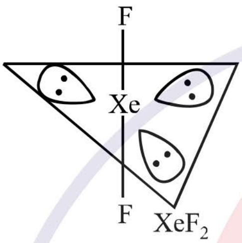
Square pyramidal

ClF_5 (sp_3d^2)

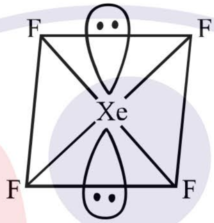


Pentagonal bipyramidal

IF_5 (sp^3d^3)

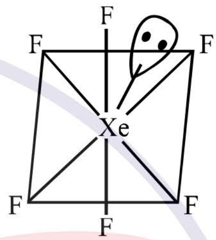


XeF_2 Linear (sp^3d)



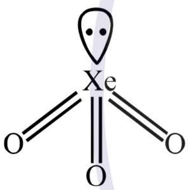
XeF_4 Square Planer

(sp^3d^2)



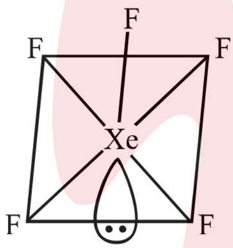
XeF_6 (sp^3d^2)

Distorted octahedral



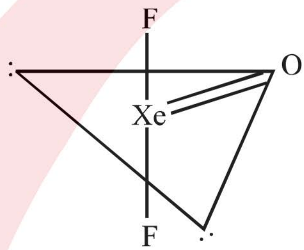
sp^3 Pyramidal

XeO_3



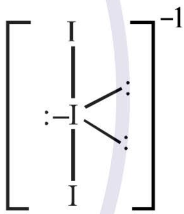
Square pyramidal

$XeOF_4$ (sp^3d^2)



$XeOF_2$ (sp^3d)

T-shaped



I_2 ($\bar{s}p^3d$)

Linear

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 ?