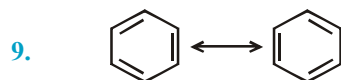


## HINTS &amp; SOLUTIONS

## EXERCISE - 1

## Single Choice

4. The conditions required for the formation of an ionic bond.  
 (i) Ionization enthalpy  $[M(g) \rightarrow M^+(g) + e^-]$  of electropositive element must be low.  
 (ii) Negative value of electron gain enthalpy  $[X(g) + e^- \rightarrow X^-(g)]$  of electronegative element should be high.
6. Here  $\Delta_{xz} = 3 - 1 = 2 > 1.7$   $\therefore$  XZ is ionic  
 $\Delta_{yz} = 2 - 1 = 1 < 1.7$   $\therefore$  YZ is covalent.
7. Cs has lowest  $IE_1$  amongst the metals and F has higher electron affinity. So Cs and F form most ionic compound.
8. In  $SF_6$ ,  $PCl_5$  and  $IF_7$  the valence shell has 12, 10 and 14 electrons. As all contain more than 8 electrons in their valence shell they are example of super octet molecules.



$\therefore$  Bond order = 1.5.

11. (D) Position of atoms are different.  
 (E) Has unpaired electrons and this is not possible since the molecule is diamagnetic.

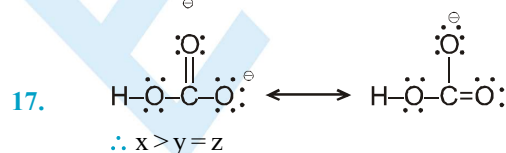
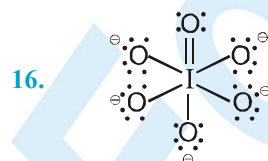
14.  $N_3^-$ ,  $(CNO)^-$  and  $(NCN)^{2-}$  all have same number of electrons i.e., 22 ; so all are isoelectronic with  $CO_2$  which also has 22 electrons.

15. Bond length  $\propto \frac{1}{\text{Bond order}}$   
 Bond order of  $CO = 3$  (as isoelectronic with  $N_2$ )  
 Bond order =  $\frac{\text{No. of bonds in all possible sides}}{\text{No. of resonating structures}}$

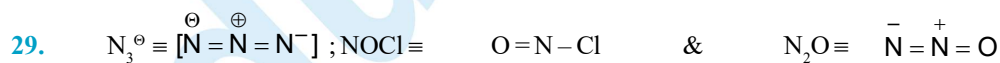
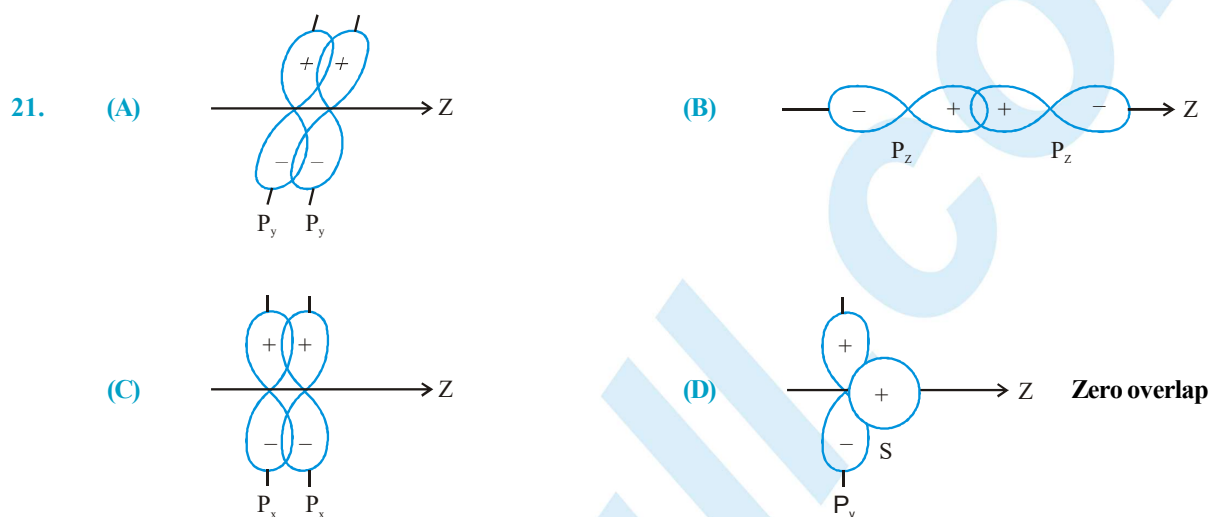
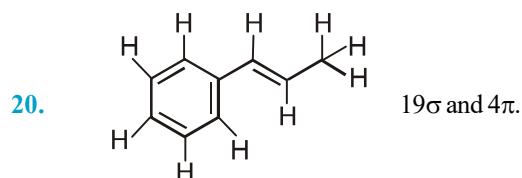
$$\text{Bond order of } CO_2 = \frac{4}{2} = 2$$

$$\text{Bond order of } CO_3^{2-} = \frac{4}{3} = 1.33$$

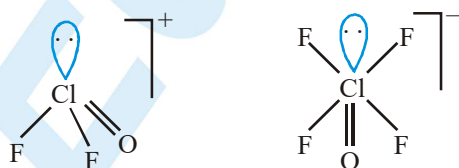
So, order of bond length of C – O is  $CO < CO_2 < CO_3^{2-}$

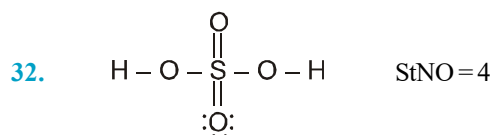


18. (A)  $\sigma$  bond is formed by axial over lapping.  
 (B) p-orbital have both axial and side ways over lapping

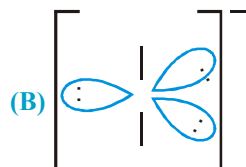
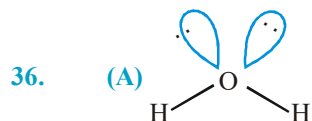


30. (A) both are  $sp^3d$   
 (B) both are  $sp^3d$   
 (C)  $[ClF_2O]^+$  is  $sp^3$  but  $[ClF_4O]^-$  is  $sp^3d^2$

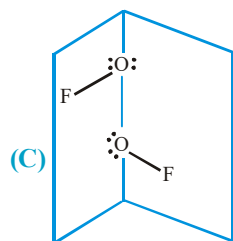




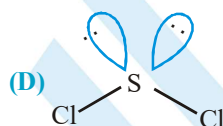
hybridization =  $sp^3$



Number of bond pairs around I = 2. Number of lone pairs around I = 3.

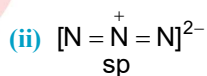
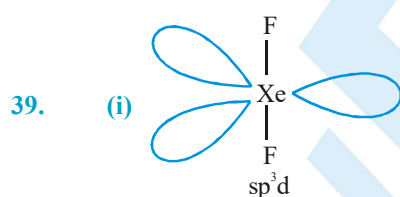
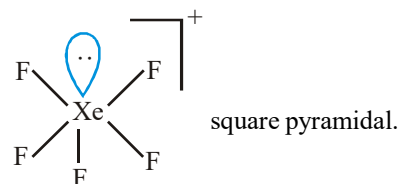
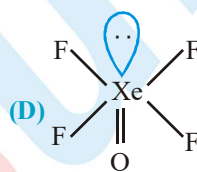


38. (A)  $\text{XeO}_3$  is trigonal pyramid.

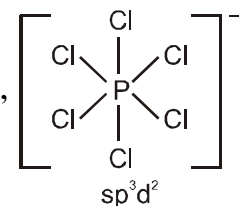


(B)  $\text{IOF}_4^+$  is see-saw.

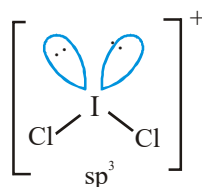
(C)  $\text{PCl}_5$  is trigonal bipyramidal.

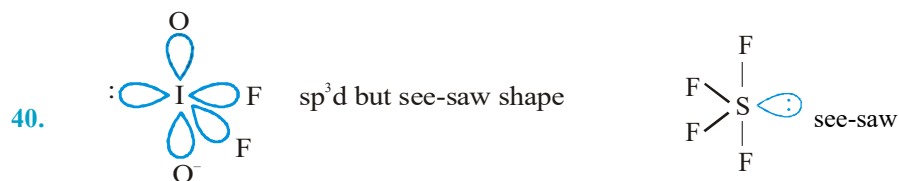


(iii)  $\text{PCl}_5$  (s) exists as  $[\text{PCl}_4]^+$  and  $[\text{PCl}_6]^-$ ,

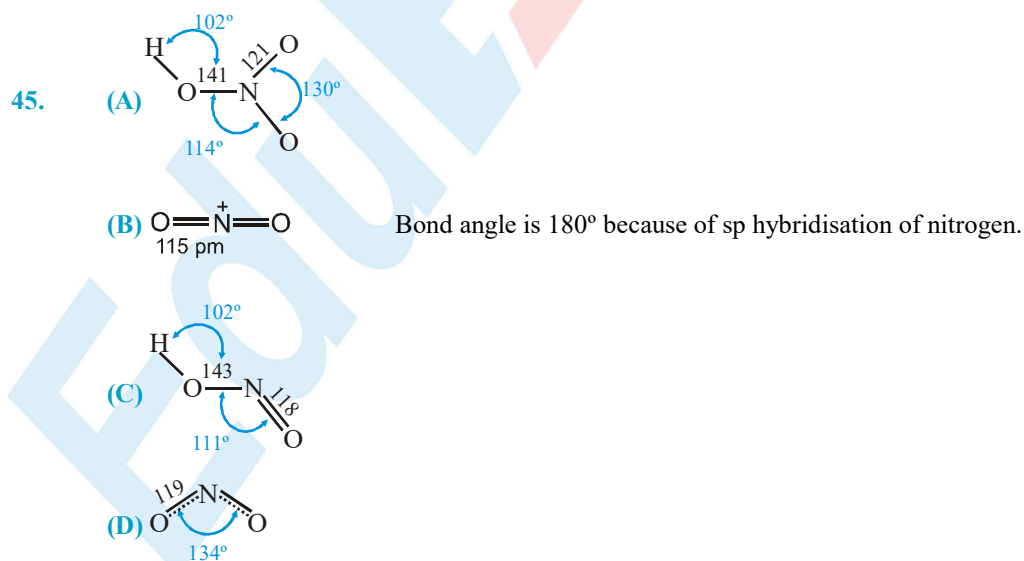
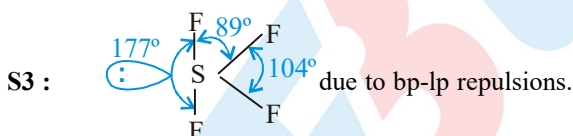
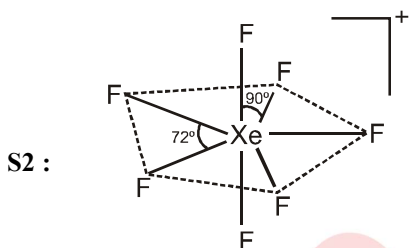
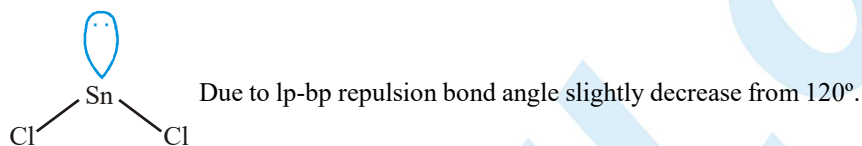
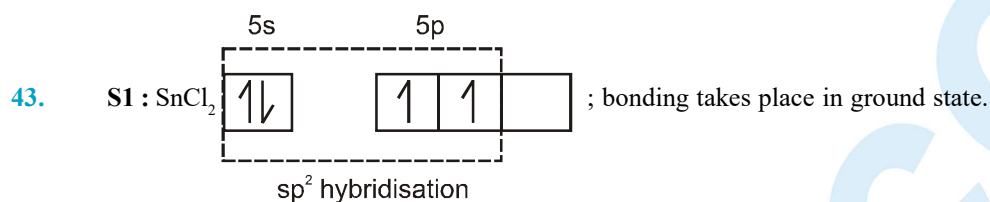


(iv)  $\text{I}_2\text{Cl}_6(\bullet) \rightleftharpoons [\text{ICl}_2]^+ + [\text{ICl}_4]^-$   
self ionisation





41. As the electronegativity of central atom increases the bond angle increases due to repulsion between bond pair and bond pair as bond pairs are more close to the central atom.



48.	Species	Bond order
	$C_2H_2$	3
	$C_2H_4$	2
	$C_2H_6$	1
	$C_2H_2Br_2$	2

49. Presence of two LP.s on Cl, distorts the bond angle. Statement 3 is against VSEPR.

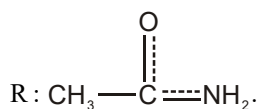
50.  $PH_3$  – No Hybridisation

$NH_3$  and  $H_2O$  bond angle is less than  $109^\circ 28'$  due to LP–BP and LP–LP repulsion.

$CH_4$  bond angle is  $109^\circ 28'$

52. P :  $CH_3 - C \equiv N$

Q :  $H - N = C = O$

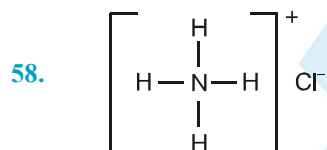


54.  $CaC_2$  exists as  $Ca^{2+}$  and  $C_2^{2-}$   $[\overset{\ominus}{C} \equiv \overset{\ominus}{C}]$ .

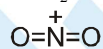
56. Hybridization does not take place without s-orbital

57.

Species	Hybridisation
$CO_3^{2-}$	$sp^2$
$XeF_4$	$sp^3d^2$
$I_3^-$	$sp^3d$
$PCl_3$	$sp^3$
$BeCl_2$	$sp$



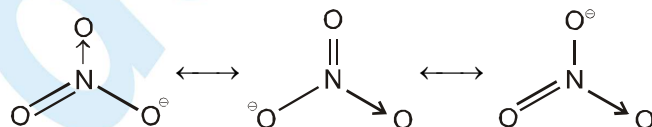
60. N atom in  $NO_2^+$  is  $sp$  hybridised while in  $NO_2^-$  and  $NO_3^-$ , it is  $sp^2$  hybridised.



Bond order = 2



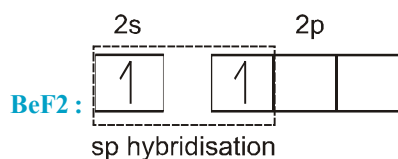
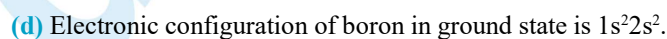
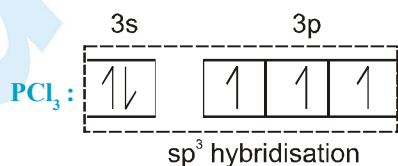
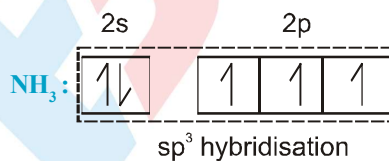
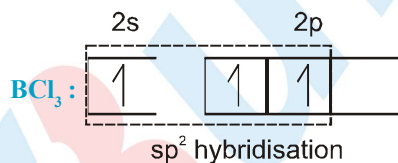
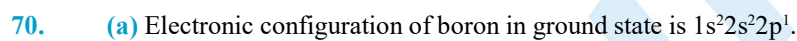
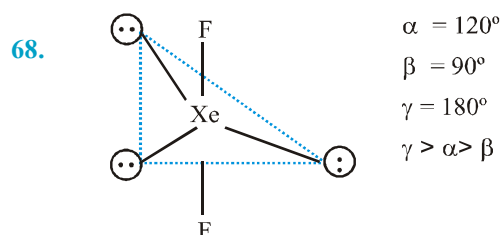
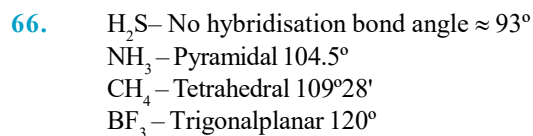
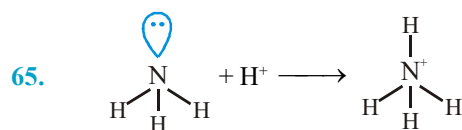
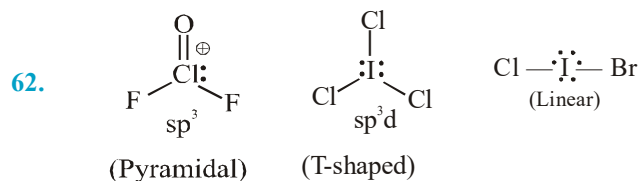
Bond order =  $\frac{2+1}{2} = 1.5$

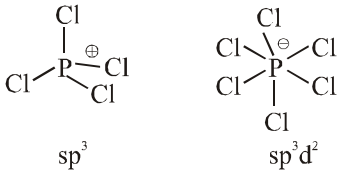
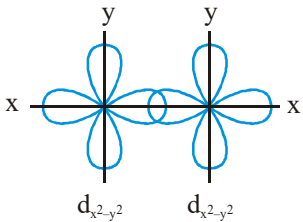
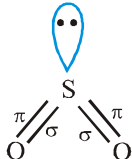


Bond order =  $\frac{2+1+1}{3} = 1.33$

Bond order  $\propto \frac{1}{\text{Bond length}}$

So, bond length order is  $NO_3^- > NO_2^- > NO_2^+$ .

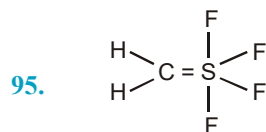
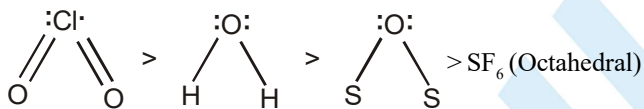


71.   
 $sp^3$   $sp^3 d^2$
75.  $O = \overset{\oplus}{N} = O$  Bond order = 2  
 $\ominus O - N = O$  Bond order = 1.5
80. The hybridization & shape of  $ClO_3^\ominus$  is  $sp^3$  & pyramidal but hybridization & shape of  $NO_3^\ominus$  is  $sp^2$  & trigonal planar.
82. (A)  $BrF_5$  contains 10 electrons in place of eight.  
 (B)  $SF_6$  contains 12 electrons in place of eight.  
 (C)  $IF_7$  contains 14 electrons in place of eight.
83. The maximum covalency of an element is equal to the number of s & p electrons in valence shell.
85. Electronegativity difference between two combining elements must be larger for ionic compound and it is the essential condition for the formation of ionic compounds. It is ionic because electronegativity difference between two combining elements is 1.8.
86.   
 $d_{x^2-y^2}$   $d_{x^2-y^2}$
87.   
 $\pi$   $\sigma$   $\sigma$   $\pi$
88. (A)  $H_2C = \overset{sp^2}{C} - \overset{sp}{C} \equiv \overset{sp}{C} - \overset{sp^2}{C} = CH_2$   
 $\downarrow$   $\downarrow$   $\downarrow$   $\downarrow$   $\downarrow$   
 $H$   $H$
- (B)  $N \equiv \overset{\sigma}{C} - \overset{\sigma}{C} \equiv \overset{\sigma}{C} - \overset{\sigma}{C} \equiv N$   
 $\downarrow$   $\downarrow$   
 $H$   $H$
- (C) In diamond each carbon atom is in  $sp^3$  hybridisation.
- (D)  $O = C = C = C = O$   
 $\downarrow$   $\downarrow$   $\downarrow$   
 $sp$   $sp$   $sp$
89. Bond energy  $\propto$  Bond order  
 Species Bond order  
 CO 3  
 $CO_2$  2  
 $CO_3^{2-}$  1.33
90.  $H - N^+ - N^+ = N^{2-}$  ; there is positive charge on two adjacent nitrogen atoms. This leads to repulsion and thus (II) increases the energy of the molecule.

92.  $\text{CH}_2 = \overset{\oplus}{\text{CH}}$   
steric No. = 2  
 $\therefore$  Hybridisation  $\text{sp}$ .

93. A fact, to be remembered.

94. (a) According to VSEPR as electronegativity of central atom decreases, bond angle decreases. So bond angle of  $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$   
(b)  $\text{C}_2\text{H}_2 > \text{C}_2\text{H}_4 > \text{CH}_4 > \text{NH}_3$  with bond pair- lone pair repulsion  
 $\text{sp} \quad \text{sp}^2 \quad \text{sp}^3 \quad \text{sp}^3$   
(c)  $\text{SF}_6 < \text{NH}_3 < \text{H}_2\text{O} < \text{OF}_2$  in this case bond angle of  $\text{NH}_3$  is highest because lp - lp repulsion is absent in it.  
(d)  $\text{ClO}_2 > \text{H}_2\text{O} > \text{H}_2\text{S} > \text{SF}_6$   
 $\text{ClO}_2$  bond angle is highest due to its  $\text{sp}^2$  hybridisation, rest all are  $\text{sp}^3$  or  $\text{sp}^3\text{d}^2$  hybridised more repulsion in double bond electrons.



Hydrogen atoms are in a vertical plane with axial fluorine atoms,  $\pi$ -bond involving a p-orbital of carbon atom must lie in equatorial plane of the molecule.

Six atoms, i.e. 2 H-atoms, C, S, and both axial F-atoms lie in one plane.

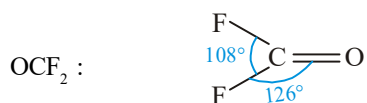
96. Due to more polarising power of Li against other members of the family.
97. Oxidation no. of N in  $\text{N}_2\text{O}_5$  is +5  
Anhydride of  $\text{HOCl}$  is  $\text{Cl}_2\text{O}$ .  
The bond length decreases with increase in difference of electronegativity.

98. The cation should be  
 $[\text{H}-\text{C} \equiv \text{N}-\text{Xe}-\text{F}]^+$   
Hybridisations  $\text{sp} \quad \text{sp} \quad \text{sp}^3\text{d}$

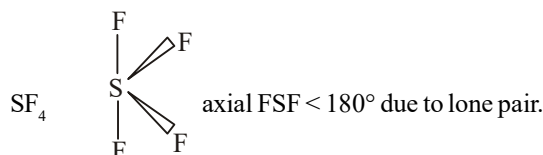




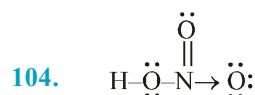
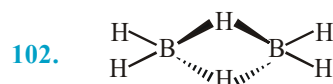
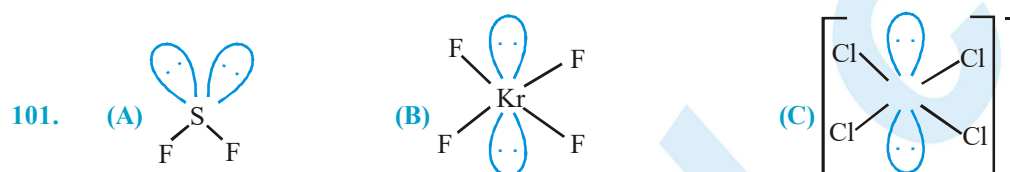
100. Generally lone pair causes more distortion than a double bond so equatorial  $\angle \text{FSF}$  in  $\text{SOF}_4 >$  equatorial  $\angle \text{FSF}$  in  $\text{SF}_4$



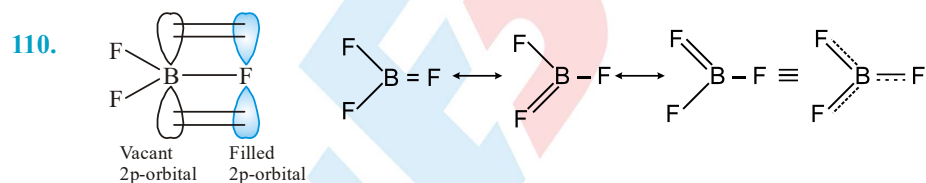
due to low bond pair bond pair repulsion because of fluorine & large repulsion due to double bond.



Similar orbitals on hybridisation can not decrease their energy due to energy conservation law



109. In  $\text{SOCl}_2$ , sulphur atom is  $\text{sp}^3$  hybridised. Due to the presence of one lone pair of electrons on 'S' atom, the molecule has distorted tetrahedral shape, i.e., trigonal pyramidal shape. This shape contains two chlorine and one oxygen atom in a triangle. The  $\text{S}-\text{O}$   $\pi$  bond is  $\text{d}\pi-\text{p}\pi$   $\pi$  bond.



Decrease in  $\text{B}-\text{F}$  bond length is due to delocalised  $\text{p}\pi-\text{p}\pi$  bonding between filled  $\text{p}$ -orbital of  $\text{F}$  atom and vacant  $\text{p}$ -orbital of  $\text{B}$  atom.

114.  $\text{N}_2^{2-}$ :  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2 \pi 2p_x^1 \pi^* 2p_y^1$ .

$$\text{B.O. } \text{N}_2^{2-} = \frac{10-6}{2} = 2. \quad ; \quad \text{B.O. } \text{O}_2 = \frac{10-6}{2} = 2.$$

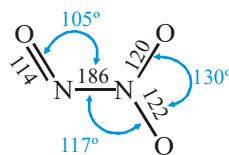
$\text{NO}^-$  isoelectronic with  $\text{O}_2$  so  $\text{B.O.} = \frac{10-6}{2} = 2$ .

All have same number of electrons (i.e. 16) so isoelectronic.

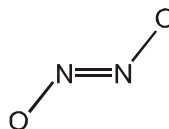
116. The electron density is zero in the nodal plane during the formation of a molecular orbital from atomic orbitals of the same atom.

118. (A) Bond order of  $N_2^+ = 2.5$  ; The bond order of  $O_2^+ 1/2(10 - 5) = 2.5$ .  
 (B) Bond order of  $F_2 = 1$  ; The bond order of  $Ne_2 = 0$ .  
 (C) Bond order of  $O_2 = 2$  ; The bond order of  $B_2 = 1$ .  
 (D) Bond order of  $C_2 = 2$  ; The bond order of  $N_2 = 3$ .
120.  $B_2$  bond order = 1 ;  $C_2$  bond order = 2 ;  $F_2$  bond order = 1 ;  $O_2^-$  bond order = 1.5  
 bond order  $\propto 1/\text{bond length}$ .
121. (A)  $NO^-$  is derivative of  $O_2$  and isoelectronic with  $O_2$ .  
 $So (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$  and 2 unpaired electrons.  
 (B)  $O_2^{2-} : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$  and no unpaired electrons.  
 (C)  $CN^-$  is derivative of and isoelectronic with  $N_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$  and no unpaired electron.  
 (D)  $CO$  is derivative of and isoelectronic with  $N_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$  and no unpaired electron.
123. (A) Stability  $O_2^+ > O_2 > O_2^-$   
 Bond order 2.5 2 1.5  
 (C) In all these molecules all electrons are paired in molecular orbitals.
126. (C)  $O_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$   
 $O_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^1)$
128. (I)  $O_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$   
 Bond order =  $1/2(10 - 5) = 2.5$ .  
 (II)  $NO$  is derivative of  $O_2$  and isoelectronic with  $O_2^+ :$   
 $so (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$   
 Bond order =  $1/2(10 - 5) = 2.5$ .  
 (III)  $N_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^1$   
 Bond order =  $1/2(9 - 4) = 2.5$ .  
 $O_2^+ , NO$  and  $N_2^+$  have same bond order i.e. 2.5 and have same magnetic property having one unpaired electron.

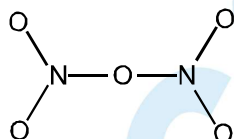
129. (A)  $\text{N}_2\text{O}_3$  Dinitrogen trioxide



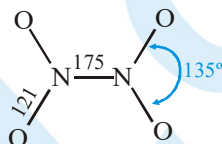
(B)  $\text{N}_2\text{O}_2^{2-}$  Hyponitrite ion



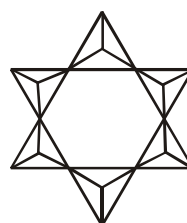
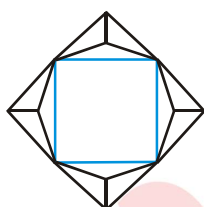
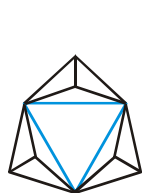
(C)  $\text{N}_2\text{O}_5$  Dinitrogen pentoxide



(D)  $\text{N}_2\text{O}_4$  Dinitrogen tetroxide

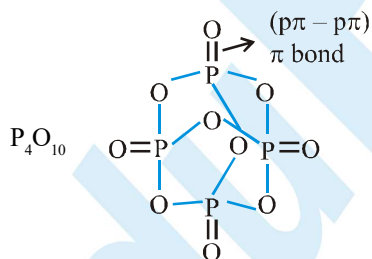


132.

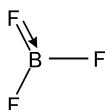


general formula of cyclic silicates is  $[\text{Si}_n\text{O}_{3n}]^{2n-}$

135.

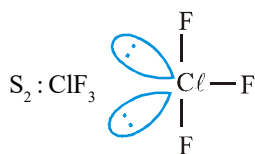


136. Partial double bond character is developed in B-F bond of  $\text{BF}_3$  (due to formation of dative  $\pi$  bond)



In other case B is  $\text{sp}^3$  hybridised (tetrahedral molecule or ion) and the possibility for  $\pi$  bonding no longer exists.

138.  $S_1$  : as it does not have d-orbitals.

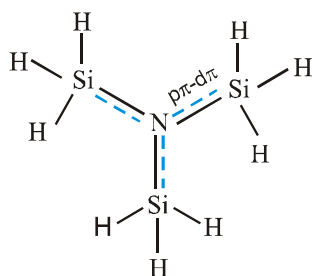


$S_3$  : In  $B_2$  mixing of the  $\sigma_g(2s)$  orbital with the  $\sigma_g(2p)$  orbital lowers the energy of the  $\sigma_g(2s)$  orbital and increases the energy of the  $\sigma_g(2p)$  orbital to a higher level than the  $\pi$  orbitals. As a result, the last two electrons are unpaired in the degenerate (having the same energy)  $\pi$  orbitals, and the molecule is paramagnetic.

In  $N_2$  the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  levels of  $N_2$  interact (mix) less than the  $B_2$  and  $C_2$  levels, and the  $\sigma_g(2p)$  and  $\pi_u(2p)$  are very close in energy.

139. Boron trimethyl is a weaker Lewis acid than the boron trihalides or monoborane. The electron donating effect of the methyl groups hinders the complex formation with trimethyl amine. Hence the bond  $N \rightarrow B$  is weakest in  $[(CH_3)_3N \rightarrow B(CH_3)_3]$ .  $Me_3N$  as donor (capacity).  $BBr_3 > BCl_3 > BF_3 \sim BH_3 > BMe_3$ .

141. There is  $p\pi-d\pi$  delocalization of lone pair of electron on nitrogen atom and empty d-orbital of silicon but not  $p\pi-p\pi$ , one of the 2s-orbital electrons jumps to the last  $P_z$  orbital and does not participate in  $sp^2$  hybridisation.



144. M.O for  $C_2 = \sigma_1 s^2 < \sigma_1^* s^2 < \sigma_2 s^2 < \sigma_2^* s^2 < \pi_2 p_x^2 = \pi_2 p_y^2 < \sigma_2 p_z^2$
- $\begin{matrix} \pi_2 p_x^2 & \pi_2 p_y^2 \\ \text{HOMO} & \text{LUMO} \end{matrix}$

It is important to note that double bond in  $C_2$  consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals  $C_2^{2-} [C \equiv C]^{2-}$ .

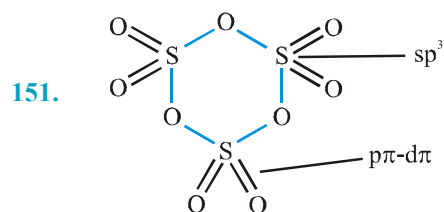
- 147.
- |   |                                     |                       |
|---|-------------------------------------|-----------------------|
|   | $NO^- > NO > NO^+$                  | (bond length)         |
| Bond order                                      | 2.0    2.5    3                     |                       |
|   | $H_2 > H_2^+ > He_2^+$              | (bond energy)         |
| Bond order                                      | 1    0.5    0.5                     |                       |
| (In $He_2^+$ more electron in antibonding MO's) |                                     |                       |
|   | $NO_2^+ > NO_2 > NO_2^-$            | (bond angle)          |
| Bond angle                                      | $180^\circ$ $133^\circ$ $115^\circ$ |                       |
|   | $O_2^{2-} < O_2^+ < O_2$            | (paramagnetic moment) |
| No. of unpaired e <sup>-</sup>                  | 0    1    2                         |                       |

148.  $He_2^+$  bond order =  $\frac{2-1}{2} = \frac{1}{2}$ ;  $O_2^-$  bond order =  $\frac{10-7}{2} = 1.5$

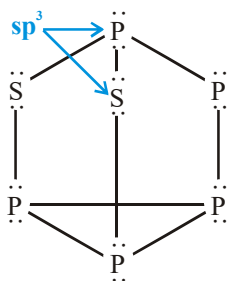
$$C_2 \text{ bond order} = \frac{8-4}{2} = 2; NO \text{ bond order} = \frac{10-5}{2} = 2.5$$

Bond order  $\propto$  bond dissociation energy.

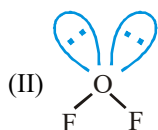
149. diamond (1.54 Å)  
graphite (1.42 Å) . ( $\perp$  to the sheets there is no covalent bonding)  
 $C_{60}$  (1.45 Å and 1.38 Å)  
benzene (1.36 Å).



152. Hybridisation is  $sp^3$ .

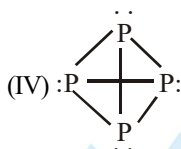


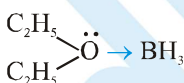
154. (I)  $[PCl_4]^+ \rightarrow sp^3$



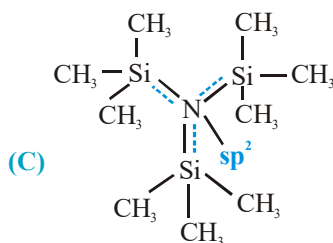
has  $\approx 102^\circ$  bond angle due to lp-lp repulsion, as bond pairs are closer to F-atoms.

(III) All have  $sp^3$  hybridisation and one lone pair.

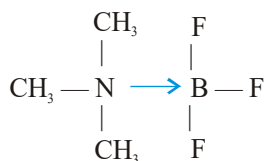


156. 

157. (A)  (B) 



- 158 In  $\text{BF}_3$  the B - F bond length is shorter than normal bond character on account of  $p\pi - p\pi$  back bonding ( $1.30 \text{ \AA}$ ). In 1 : 1 complex there is no  $p\pi - p\pi$  back bonding and hence the B-F bond length is longer, ( $1.35 \text{ \AA}$ ).



Steric number                      4                      4

Hence both N and B have tetrahedral geometry with  $sp^3$  hybridisation.

- 161  $\text{N}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$

The bond order of  $\text{N}_2$  is  $1/2(10 - 4) = 3$ .

$$\text{N}_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^1$$

The bond order of  $\text{N}_2^+$  is  $1/2(9 - 4) = 2.5$ .

$$\text{O}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$$

The bond order of  $\text{O}_2$   $1/2(10 - 6) = 2$ .

$$\text{O}_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^1)$$

The bond order of  $\text{O}_2^-$   $1/2(10 - 7) = 1.5$ .

$\text{NO}^+$  derivative of  $\text{O}_2$  and isoelectronic with  $\text{O}_2^{2+}$ ; so  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2)$

The bond order of  $\text{NO}^+$   $1/2(10 - 4) = 3$ .

$\text{NO}$  derivative of  $\text{O}_2$  and isoelectronic with  $\text{O}_2^+$ ;  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2), (\pi^* 2p_x)^1$

The bond order of  $\text{NO}$  is  $1/2(10 - 5) = 2.5$ .

bond order  $\propto 1/\text{bond length} \propto \text{bond dissociation energy}$ .

- 163  $\text{OF}$  is derivative of  $\text{O}_2$  and isoelectronic with  $\text{O}_2^-$ .

$$\text{So } (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^1)$$

The bond order of  $\text{OF}$   $1/2(10 - 7) = 1.5$ .

- 164 (A)  $\text{H}_2\text{O}_2 = 1.48 \text{ \AA}$  due to repulsions between non-bonded pairs of electron on O-atoms and  $\text{O}_2\text{F}_2 = 1.217 \text{ \AA}$ .

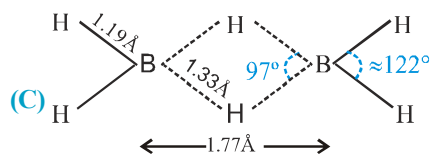
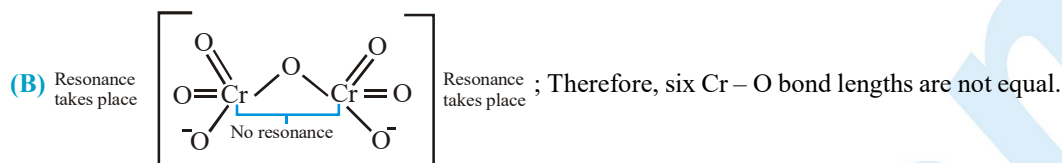
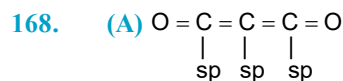
(B) In  $\text{O}_2^{2-}$  very slightly increases due to charge (-ve) on two O atoms.

	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons
$\text{O}_2^+$ (dioxygenyl)	2.5	112.3	1
(C) $\text{O}_2$ (dioxygen)	2.0	120.07	2
$\text{O}_2^-$ (superoxide)	1.5	128	1
$\text{O}_2^{2-}$ (peroxide)	1.0	149	0

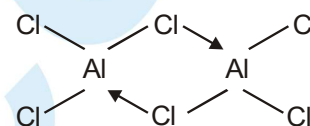
165. Bond order of  $\text{N}_2 = 3$  bond order of  $\text{N}_2^+ = 2.5$

B.O. of  $\text{O}_2 = 2$ .

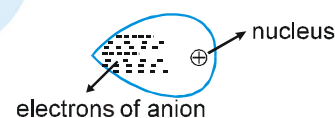
B.O. of  $\text{O}_2^+ = 2.5$



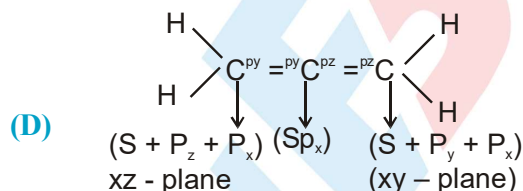
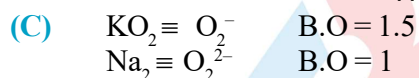
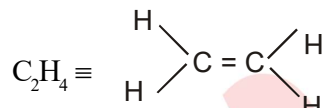
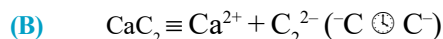
This is an example of 3-centre  $2e^-$  bond which is also known as Banana bond. But  $\text{Al}_2\text{Cl}_6$  have covalent bond only and there is no electron deficient bonding as depicted in the given structure.



(D)  $\text{AgI}$  is bright yellow coloured compound due to the polarisation of anion,  $\text{I}^-$ . The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.



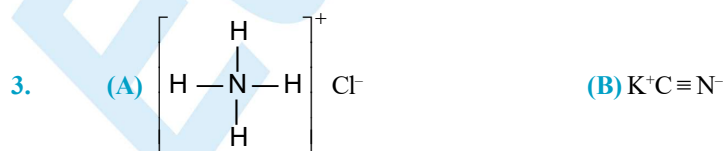
$\text{O}=\text{N}-\text{Cl}$  there is a double bond between N and 'O' atom

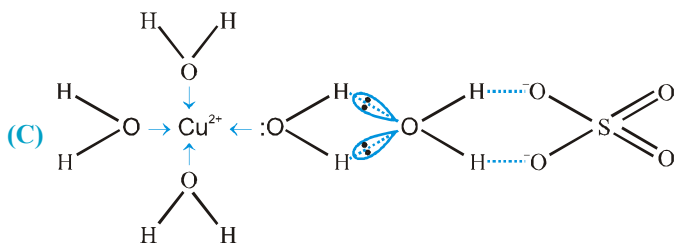


## EXERCISE - 2

### Part # I : Multiple Choice

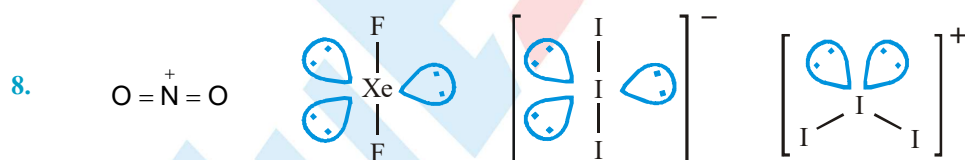
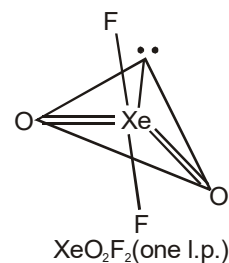
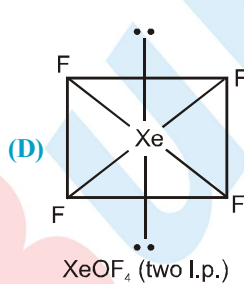
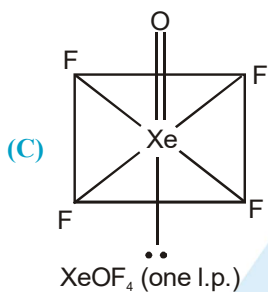
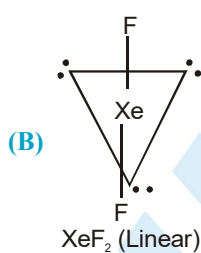
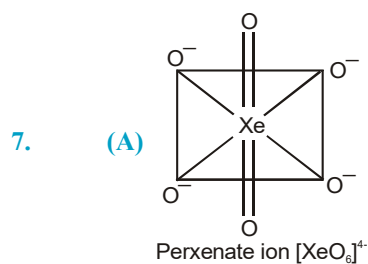
1. (A) is incorrect, as ionic compounds have higher melting points as well as higher boiling points due to strong electrostatic force of attraction between the ions. (B), (C) and (D) are properties of ionic compounds.



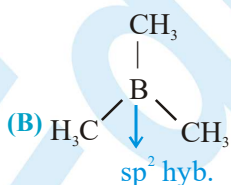


(D)  $\text{Na}^+\text{O}^-\text{H}$

4.  $\text{H}-\text{C}\equiv\text{C}-\text{CH}_3$   
The two  $\pi$  bonds are in mutually perpendicular plane. The terminal C-atom is  $\text{sp}^3$  hybridised.



10. (A) Due to the presence of lone pair bond angle decreases.

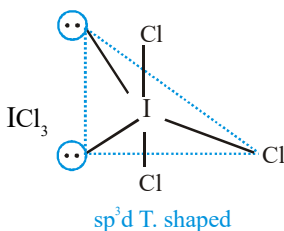


(C)  $\text{NH}_4\text{Cl}$  is an ionic compound and 'N' is in  $\text{sp}^3$  hybridisation.

(D)  $\text{S}_8$  molecule has 16 electron pairs left behind after the bonding.



11. B and C  $\Rightarrow$  Drago's rule,



12. The incorrect Lewis diagram are (A) and (C) because octet of O and S are incomplete respectively .

15. (b) If X-axis is internuclear axis, then it will result in  $\pi$  bond.

(c) It will result in  $\sigma$  bond.

(d) & (e) It shows zero overlap with no bond formation.

16.  $C^* \rightarrow 1s^2 2s^1 2p^3$  4 unpaired electron  $\therefore$  4 bonds

$B^* \rightarrow 1s^2 2s^1 2p^2$  3 unpaired electron  $\therefore$  3 bonds

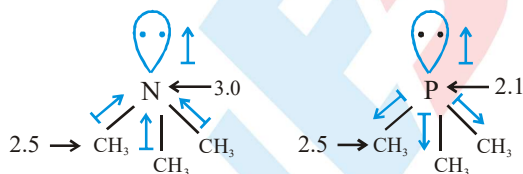
$I^* \rightarrow 5s^2 5p^4 5d^1$  3 unpaired electron  $\therefore$  3 bonds

$P^* \rightarrow 3s^2 3p^3$  3 unpaired electron  $\therefore$  3 bonds

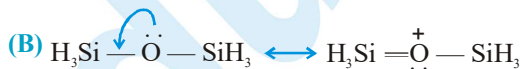
\* represent excited state

17. It is the orbital that undergo hybridisation and not the electrons. For example , for orbitals of nitrogen atom ( $2s^2 2p_x^1 2p_y^1 2p_z^1$ ) belonging to valency shell when hybridise to form four hybrid orbitals , one of which has two electrons (as before) and other three have one electron each. It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

20. (A) Nitrogen is more electronegative than phosphorus.



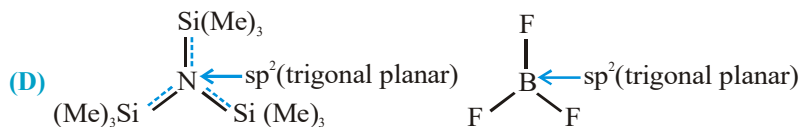
So, dipole moment of trimethylamine is greater than trimethyl phosphine.



In trisilyl ether the lone pair of electron on oxygen atom is less easily available for donation because of  $p\pi-d\pi$  delocalisation due to presence of the vacant d-orbital with Si. This however is not possible with carbon in  $CH_3-O-CH_3$  due to the absence of d-orbital making it more basic.

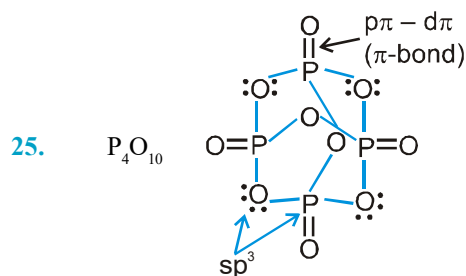
(C) Bond order of  $C_2$  and  $O_2$  are same i.e., 2. In  $C_2$  molecules both bonds are  $\pi$ -bonds whereas, there is one  $\sigma$  and one  $\pi$ -bond in  $O_2$  molecule

$C_2 = 131 \text{ pm}$  ;  $O_2 = 121 \text{ pm}$ .

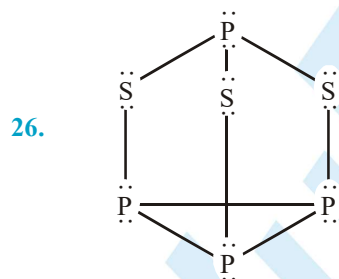


22.  $(\text{CH}_3)_2\ddot{\text{O}}\text{:}$  can act as lewis base but  $(\text{SiH}_3)_2\text{O}$  &  $(\text{SiH}_3)_3\text{N}$  can not, as one pairs on O & N are delocalised in to empty orbitals of Si.

24. In  $\text{FO}^+$  total no. of electrons = 16, so bond order will be 2.  
In  $\text{FO}^-$  total number of electrons = 18, so bond order will be 1.



The P – O bond lengths shows that the bridging bonds on the edges are 1.60 Å but the P = O bonds on the corners are 1.43 Å and this P = O is formed by  $p\pi - d\pi$  back bonding. A full p-orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P – P bonds.



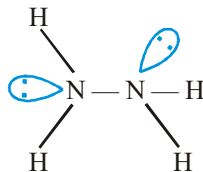
28. Fullerene are cage like molecules.  $\text{C}_{60}$  molecule has a shape like soccer ball and called **Buckminsterfullerene**.

It contains twenty 'six-membered rings' and twelve 'five membered rings'. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo  $\text{sp}^2$  hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon atom is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C – C distance of 143.5 pm and 138.3 pm respectively.

30.  $\text{Cl}_2\text{O} > \text{F}_2\text{O}$  and  $\text{F}_2\text{O} < \text{H}_2\text{O}$   
 $111^\circ \quad 102^\circ \quad 102^\circ \quad 104^\circ$   
 $\text{NO}_2^+ > \text{NO}_2^-$   
 $\text{sp} \quad \text{sp}^2$

$\text{AsI}_3 > \text{AsBr}_3 > \text{AsCl}_3$  (due to size of halogen)

31. (A) Structure is similar to that of ethane. Each N atom is tetrahedrally surrounded by one N, two H and a lone pair. The two halves of the molecules are rotated  $95^\circ$  about N–N bond and occupy a gauche (non-eclipsed) conformation. The bond length is 1.45 Å.



(B) Has partial double bond character due to  $p\pi$ - $d\pi$  delocalisation.

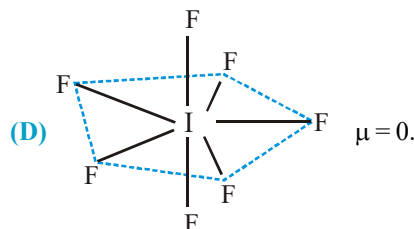
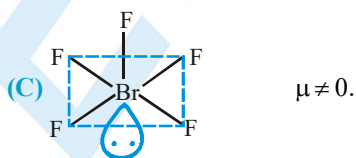
(C)  $\text{OF}_2 = 103^\circ$  (approximate) and  $\text{OCl}_2 = 112^\circ$  (approximate).

(D) Exist in polymeric structure as in solid state.

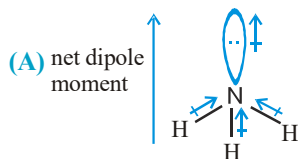
33. (A)  $\text{O}_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$   
 (B) NO is derivative of  $\text{O}_2$ :  $\text{NO}(\text{O}_2^+) (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$   
 (C)  $\text{O}_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$   
 (D)  $\text{B}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^1 = \pi 2p_y^1) (\sigma p_z)^0$

37. (A) It results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole.  
 (B) In general, greater the number of  $(n-1)d$  and  $ns$  electrons, stronger is the resultant bonding.  
 (C) Strength of metallic bond depend on the type of hybrid orbitals participating in metallic bonding.  
 (D) As the size of atom increases the attraction between the positive part of the atom and delocalised electrons decreases and thus the strength of the metallic bond decreases.

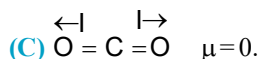
39. (A) I – Cl, linear and polar because of the difference in the electronegativities of iodine and chlorine.



40



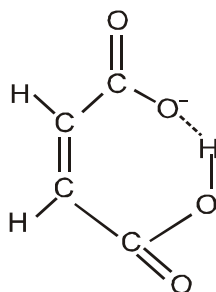
(B) Dipole moment is a vector quantity as it depends on the magnitude and the direction.



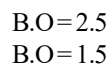
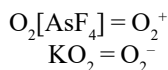
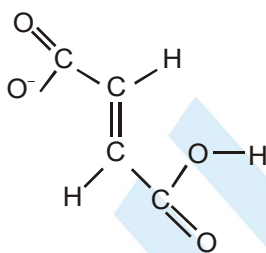
(D) As a result of polarisation in covalent bond which arises due to the difference in the electronegativities of combining atoms, the molecule possesses the **dipole moment**.

42

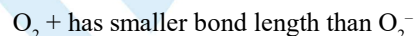
maleic acid



fumaric acid



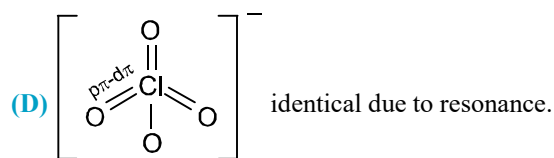
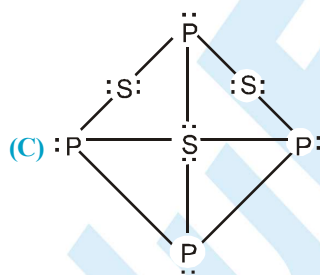
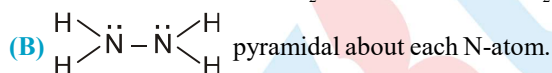
so



Greater the size of the halogen atom greater will be bond angle.

43

(A) Boiling point of  $\text{ICl} > \text{Br}_2$  as  $\text{ICl}$  is polar and  $\text{Br}_2$  is non-polar in nature.



44

(A)  $\text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$  (order of B.Pt)

(B) As  $\text{D}_2\text{O}$  has higher molecular mass than  $\text{H}_2\text{O}$  so its density is more.

(C)  $\text{Mn} \rightarrow 4s^2 3d^5$

$\text{Ca} \rightarrow [\text{Ar}] 4s^2$

$\text{Sr} \rightarrow [\text{Kr}] 5s^2$

$\text{Rb} \rightarrow [\text{Kr}] 5s^1$

Refer notes

(D)  $\text{H}_2 \rightarrow$  weak VDW forces

$\text{CO}_2 \rightarrow$  weak VDW force but stronger than  $\text{H}_2$ .

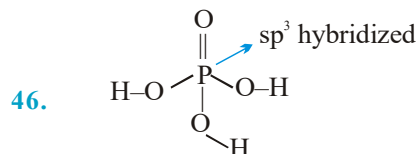
$\text{H}_2\text{O} \rightarrow$  H-bonding.

45.  $\text{S}_2\text{O}_3^{2-}$  ion :

Individual O.N. of S atoms = +6 and -2. Average O.N. = +2

$\text{SbH}_3$  has higher bp than  $\text{NH}_3$ , due to vander waal forces.

In hydric acids, the acidity increases down the group while for oxyacids, the acidity decreases down the group.

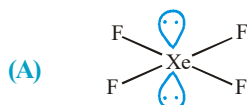


The P = O contain one  $p\pi-d\pi$  bond. The  $\text{PO}_4^{3-}$  ion show resonance.

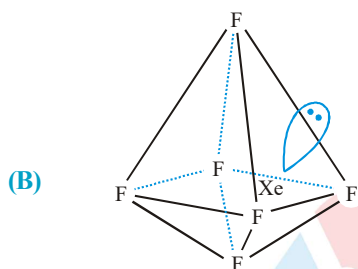
Due to the presence of H-bonded to O, it show intermolecular H-bonding due to which it is syrupy.

47. The critical temperature depends on the magnitude (of strength) of intermolecular force of attraction between the molecules. If a molecule has dipole moment it means there is dipole dipole attraction between the molecules and thus it will affect the critical temperature.

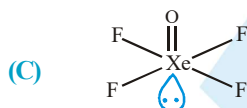
48. Polarity depend on net dipole moment. If dipole moment  $\mu = 0$  it is nonpolar.



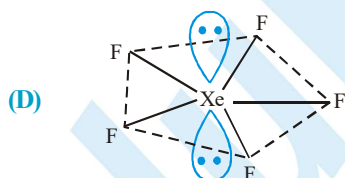
$\text{XeF}_4$   $\mu = 0$  non polar



$\text{XeF}_6$   $\mu \neq 0$  polar



$\text{XeOF}_4$   $\mu \neq 0$  polar



$\text{XeF}_5^-$   $\mu = 0$  non polar

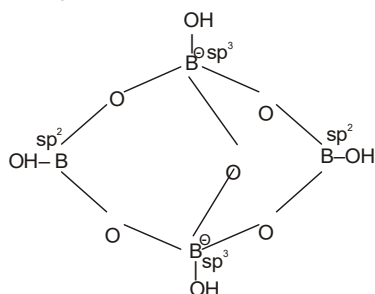
49. (A) Ethyne being non-polar is more soluble in acetone.

(B)  $\text{CD}_3\text{F}$  is more polar than  $\text{CH}_3\text{F}$ . In  $\text{CD}_3\text{F}$ , C-D bond is more polar as deuterium is more electropositive than hydrogen.

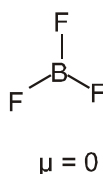
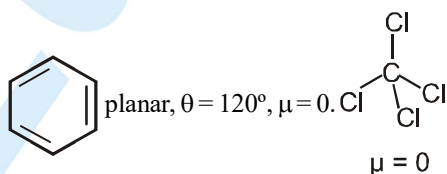
(C) Silyl isocyanate ( $\text{SiH}_3\text{NCO}$ ) is linear in shape because of  $p\pi-d\pi$  delocalisation of lone pair of electrons on nitrogen. While in methyl isocyanate ( $\text{CH}_3\text{NCO}$ ) there is no  $p\pi-d\pi$  delocalisation of electron as carbon does not have empty d-orbital and thus is bent in shape.

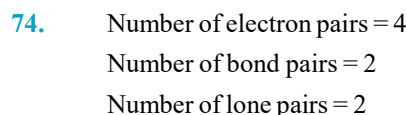
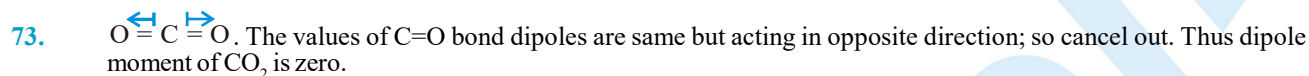
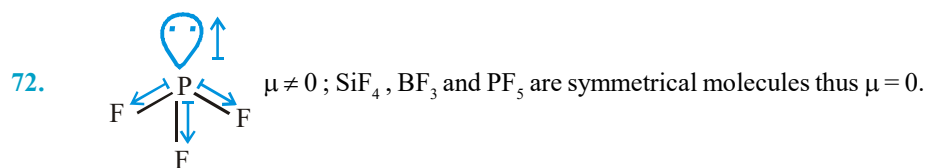
In  $\text{CH}_2=\text{C}=\text{C}=\text{CH}_2$ , the 2H-atoms on one C-atom lie in a plane perpendicular to the plane in which 2H-atoms on other C-atom lie.

50. The correct formula of borax is  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ . The structure of anion is :

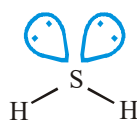


53. As charge on cations increases, their polarising power increases and thus covalent character increases.
- $$\text{Li}^+\text{Cl} < \text{Be}^{2+}\text{Cl}_2 < \text{BCl}_3 < \text{C}^{4+}\text{Cl}_4$$
54. Increase in oxidation state ( $\text{Ni}^{4+}$ ) increases the polarising power of cation and thus increases the polarisation of  $\text{Br}^-$  ion.
55. Because of high charge density on  $\text{Sn}^{4+}$  it has high polarising power and thus leads to greater polarisation of anion i.e., greater distortion of electron clouds of the  $\text{Cl}^-$  ions. So  $\text{SnCl}_4$  is most covalent.
57. The strength of metallic bonds depends upon the number of mobile electron(s) per atom. Sodium has only one mobile electron per atom where as iron has 8 mobile electrons per atom.
59. Cu, Ag, Zn are solids at room temperature where as mercury is liquid.
61. As size of cations increase, their polarising power decrease and thus ionic character increase.
63.  $\text{Sn}^{4+}$  has highest polarising power amongst  $\text{Na}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{4+}$  and  $\text{Al}^{3+}$  because of smaller size and higher charge. So  $\text{SnCl}_4$  is most covalent and thus has least melting point.
64. Metallic bond results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole.
65.  $\text{AgI}$  is less soluble than  $\text{AgF}$  due to covalent nature.  $\text{LiI}$  is more soluble than  $\text{LiF}$  due to high size difference of ions more ionic nature, more melting point. Higher the charge density, larger will be the hydrated radii.
66. Polarisation of the  $\text{I}^-$  by the  $\text{Cu}^{2+}$  results in the transference of an electron towards  $\text{Cu}^{2+}$  makes it as oxidising agent and  $\text{I}^-$  as a reducing agent, reduces  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  and itself oxidised to  $\text{I}_2$ .
67. (A)  $\text{N}_2$  contains one  $\sigma$  and two  $\pi$  bonds but  $\text{C}_2$  contains only two  $\pi$  bonds as four electrons are present in bonding  $\pi$  molecular orbitals.  
 (B)  $\text{Cu}^{2+}$  has higher hydration energy than  $\text{Cu}^+$  so  $\text{Cu}^{2+}$  is more stable than  $\text{Cu}^+$ . Moreover,  $\text{Cu}^+$  undergoes disproportionation.  $2\text{Cu}^+ \rightarrow 2\text{Cu}^{2+} + \text{Cu}$ . (a fact)  
 (C) Can be explained by electron sea model as it is due to the presence of mobile electrons.
68. Larger anion has higher polarisability.
70. Dipole moment  $\propto \frac{1}{\text{bond angle}}$
71. Symmetrical molecules have zero dipole moment.

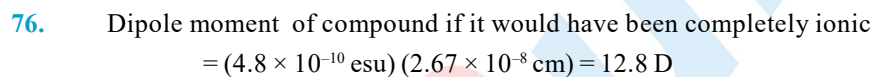
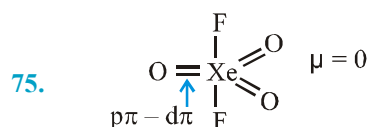




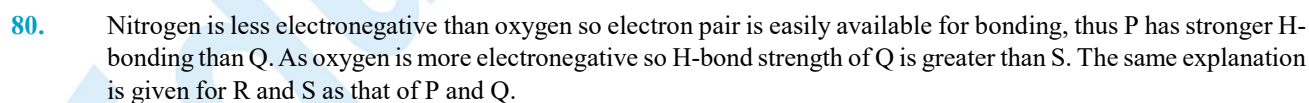
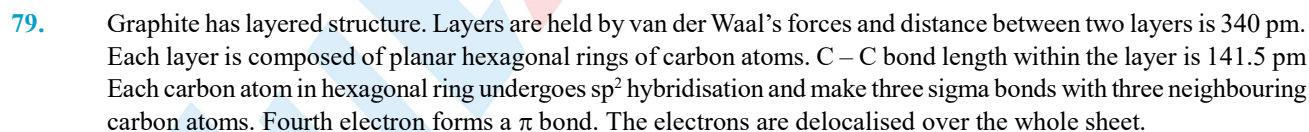
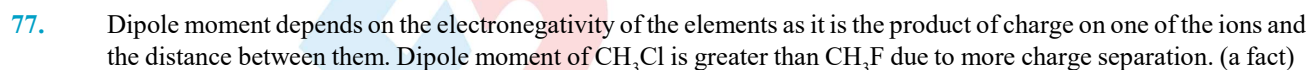
So, according to VSEPR theory to have minimum repulsions it acquires bent shape as shown below.



It is unsymmetrical molecule thus it will have some dipole moment.



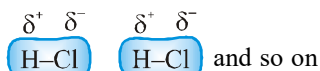
$$\text{so \% ionic character} = \frac{4.0}{12.8} \times 100\% = 31.25 \%$$





82. All molecules have London dispersion force because of number of polarizable electrons.  
Non polar molecules have only London dispersion force because of polarisable electron. Benzene is non polar molecule.

Polar molecules have dipole-dipole attraction in addition to London dispersion force.



Molecules with, O-H, N-H, or F-H bond have hydrogen bonding in addition to London dispersion force.

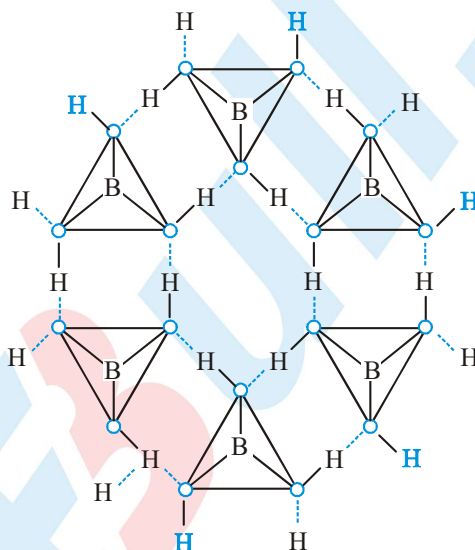
Molecule  $\text{ICl}$  is polar, so in addition to London dispersion force it has dipole-dipole attraction also.

84. London forces are extremely short range in action and the weakest of all attractive forces.  
The order of strength of bonds/ forces is ionic bond > covalent bond > hydrogen bond > London force.

86. (A) A fact

(B) In the solid state and in liquid HF, the  $\text{HF}_2^-$  ion is held together by hydrogen bonding. In aqueous solutions there is hydrogen bonding but each HF molecule forms hydrogen bonds with the much more prevalent  $\text{H}_2\text{O}$  present, instead of with other HF molecules and  $\text{H}_3\text{O}^+$  and  $\text{F}^-$  are much more likely to be formed.

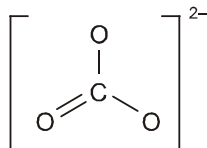
(C)  $\text{H}_3\text{BO}_3$  (solid) has inter molecular hydrogen bonding.



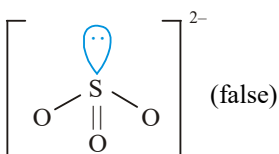
88. As molecular weight increases, magnitude of Van der Waal's force of attraction increases.  
Therefore, boiling point increases. Though  $\text{NH}_3$  has strong H-bonding but boiling point of  $\text{SbH}_3$  is highest due to highest molecular weight. Boiling point  $\text{NH}_3 = 238.5 \text{ K}$  and  $\text{SbH}_3 = 254.6 \text{ K}$ .

89. (A) intermolecular hydrogen bonded. (true)

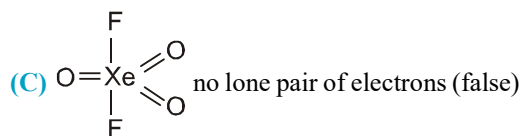
(B) structure of anions are different  $\text{CO}_3^{2-}$  – trigonal planar ( $\text{sp}^2$ )



$\text{SO}_3^{2-}$  – trigonal pyramidal ( $\text{sp}^3$ )



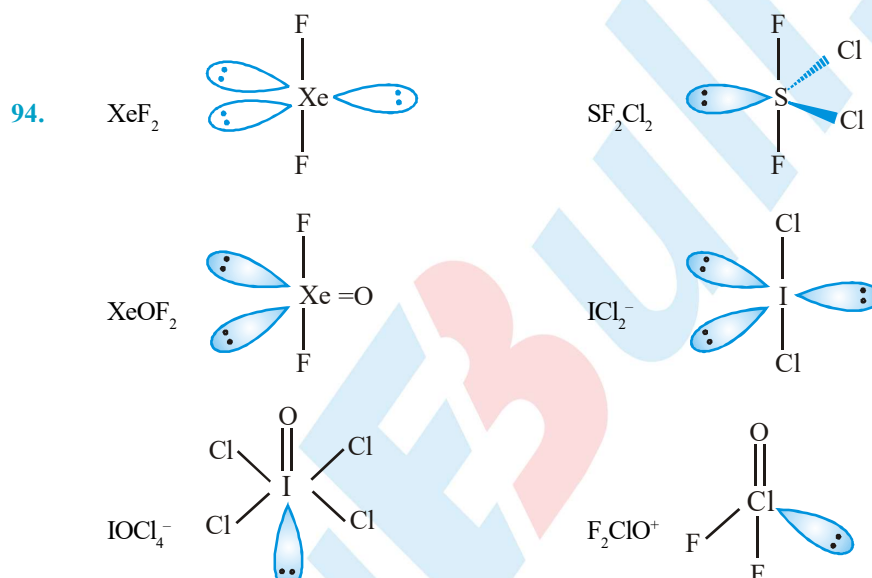
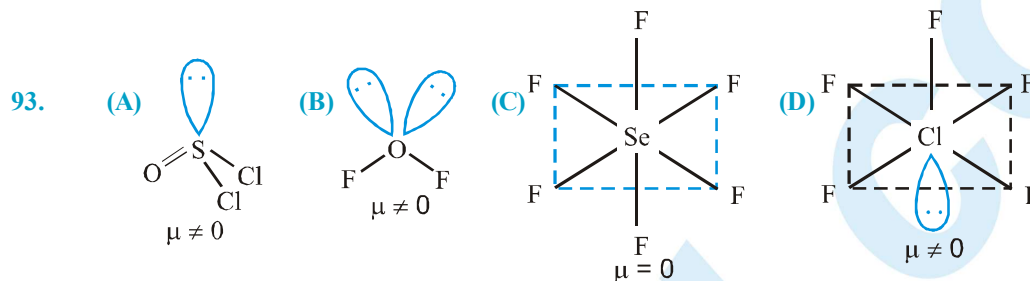




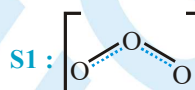
(D) True.  $D_2O = 374.4\text{ K}$ ;  $H_2O = 373.0\text{ K}$

90. (i)  $H_2O$  has highest boiling point because of H-bonding.

(ii) Boiling point also depends on the magnitude of van der Waal's force of attraction, which in turns depends on molecular weight of the compounds. Thus the correct order is  $H_2O > H_2Te > H_2Se > H_2S$ .



99. Fluorine is more electronegative but dipole moment is the product of charge and distance between combining atoms (covalently bonded); due to more charge separation in  $CH_3Cl$ , it has higher dipole moment.

100. S1 :  Due to resonance, both bonds are equal.

S2 : Hydration of ions due to force of attraction between ion and water molecule. Which is a dipole.

S3 : Due to intermolecular H-bonding, boiling point increases.

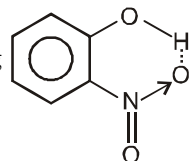
S4 : A symmetrical molecule with identical bonds have zero dipole moment.

102.  $S_1$  : Due to intermolecular H-bonding in HF it boils at higher temperature than HCl  
 $S_2$  : Mol. wt. of HBr < Mol. wt. of HI  
 $S_3$  : Bond order of  $N_2$  is more than  $N_2^+$ .  
 $S_4$  : Molecular mass of  $F_2$  is less than that of  $Cl_2$

103. Strength of H-bond depends on following factors.

- (i) Electronegativity of element covalently bonded to hydrogen atom.  
 (ii) Size of electronegative element.  
 (iii) Ease of donation of lone pair of electrons by electronegative element.

104. It has intramolecular H-bonding



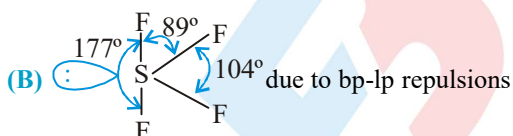
106. (A) As  $\delta^+$  charge on central atom increases, the attraction between  $\delta^+$  and  $\delta^-$  increases and thus Xe-F bond length decreases. The correct order is  $XeF_2 > XeF_4 > XeF_6$   
 (B)  $PH_5$  can not undergo  $sp^3d$  hybridisation as there is much large difference in size of s, p and d orbitals.  $PH_5$  does not exist as no partial positive charge develops on P atom.  
 (C) Dipole moment of  $CH_3Cl$  is greater than  $CH_3F$  due to greater charge separation on carbon and chlorine atoms in  $CH_3Cl$ .  
 (D) it is a correct order.

The strength of hydrogen bond depends upon :

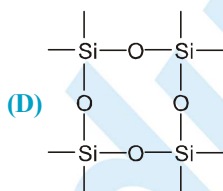
- (i) size (ii) electronegativity and (iii) ease of donation of electron pair by electronegative element.

Higher the value of electronegativity and smaller the size of the covalently bonded atom to H atom stronger is the hydrogen bonding.

107. (A) in  $S_8$  hybridisation of each S-atom is  $sp^3$ , in  $P_4$  hybridisation of each P-atom is  $sp^3$



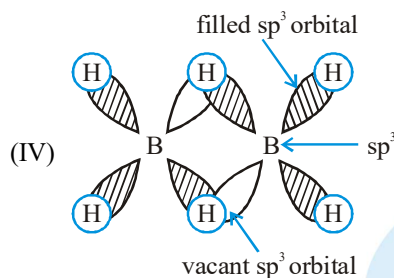
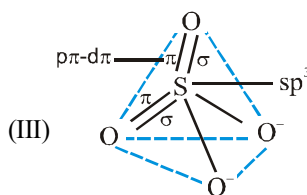
- (C) Inter molecular H-bonding ( $PO_4^{3-}$  groups are bonded by many H-bonds)



108. (I)

As a result of H-bonding, number of sulphuric acid molecules are associated to form cluster. Hence it has high boiling point and viscosity.

(II) All S — O bond lengths are equal due to resonance.



110. **S1** : Polarising power of a cation is inversely proportional to its size.

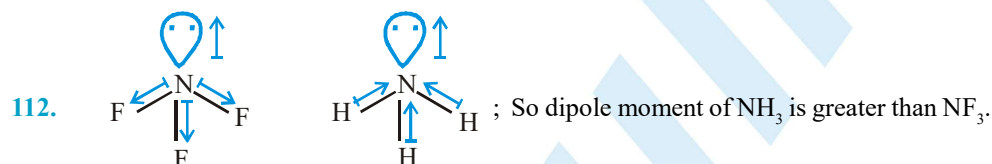
**S2** :  $\text{H}_2^+ : \sigma 1s^1$       B.O. =  $\frac{1}{2}$

$\text{He}_2^+ : \sigma 1s^2 \sigma^* 1s^1$       B.O. =  $\frac{1}{2}$

But  $\text{He}_2^+$  has electron in antibonding molecular orbital so its is unstable.

**S3** : H-bond formation requires the availability of lone pair of electron.

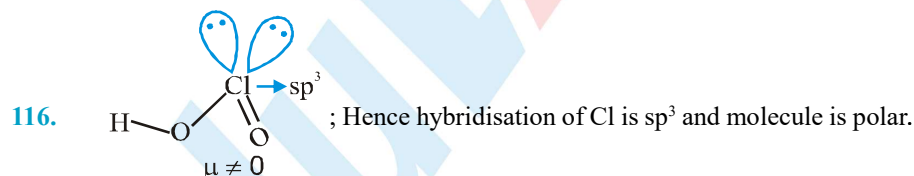
**S4** : In  $\text{Cl}_2\text{O}$ , the bond angle is more than  $109^\circ 28'$  due to steric repulsion.



113. This is based on the decreasing electronegativity difference between H (2.1) and Sb (1.9), As (2.0), P (2.1) and N (3.0).

114. van der Waal's forces  $\propto$  molecular weight. So AgBr will have maximum van der Waals forces.

115. (C) Both compounds have intermolecular H-bonding amongst themselves and with water.



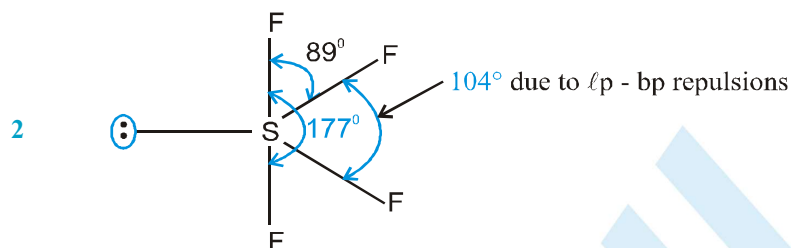
117. Polarity depend on net dipole moment. If dipole moment  $\mu = 0$  it is nonpolar.

In	$\text{XeF}_4$	$\mu = 0$	non polar ;	$\text{SO}_3$	$\mu = 0$	non polar
	$\text{XeOF}_4$	$\mu \neq 0$	polar ;	$\text{ICl}_4^-$	$\mu = 0$	non polar

118. In  $\text{CH}_4$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{S}$  the central atoms are not more electronegative ; hence do not form hydrogen bonds with itself and other molecule. In  $\text{N}_2\text{H}_4$  the nitrogen is more electronegative and thus is able to form hydrogen bond with itself and other molecules like water.

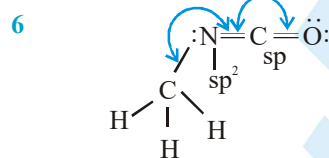
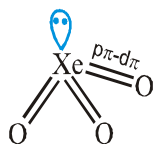
122. In pure phosphoric acid the  $\text{PO}_4^{3-}$  groups are bonded together through many hydrogen bonds.
123. HF is least volatile (i.e. high boiling point) due to strong intermolecular hydrogen bonding.
124. Boiling point of  $\text{SbH}_3$  is greater than  $\text{NH}_3$ . The higher boiling point of  $\text{SbH}_3$  is attributed to higher van der Waal forces because of its higher molecular weight. (a fact)
125. (A) Like hydrated copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in which one water molecule is hydrogen bonded to coordinated water molecule, one water molecule is coordinated to lone pair of electrons on  $\text{SnCl}_2$  and the other is hydrogen bonded to coordinated water molecule.

Part # II : Assertion & Reason



3. **Statement-1** : It is correct statement because all three p-orbitals are involved in  $\text{sp}^3$  hybridisation and thus no p-orbital is left for side wise overlapping.

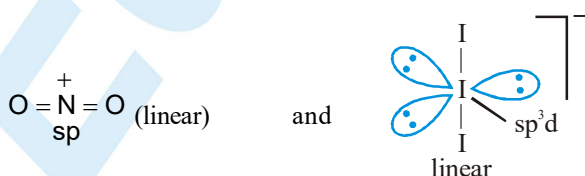
**Statement-2** :  $\text{XeO}_3$  is  $\text{sp}^3$  hybridised and Xe form three double bonds through  $\text{p}\pi\text{-d}\pi$  overlapping.



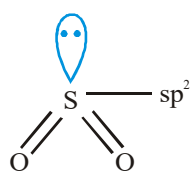
8. **Statement-1** : To have minimum repulsion between the  $\text{I}=\text{O}$  and the lone pair of electrons (has greater repulsive effect), the lone pair is opposite to the  $\text{I}=\text{O}$  bond.

**Statement-2** : correct statement.

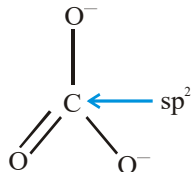
9. Statement-1 and Statement-2 both are correct statement and Statement-2 is the correct statement of Statement-1, e.g.,  $\text{NO}_2^+$  and  $\text{I}_3^-$  have different hybridisation but on account of stability they have linear shape as given below.



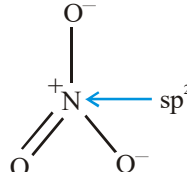
10.  $S_1$  :  $SO_2$ ,  $NO_3^-$  and  $CO_3^{2-}$  have same number of electrons (i.e. 32) but have different molecular geometry.



(bent)



(trigonal planar)



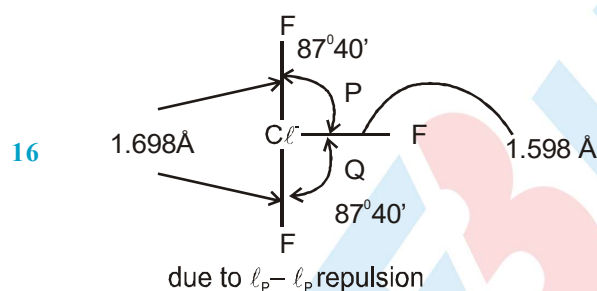
(trigonal planar)

$S_2$  : The d and f-orbitals do not shield the nuclear charge very effectively. Therefore, there is significant reduction in the size of the ions, just after d or f orbitals have been completely filled. This is called lanthanide contraction.

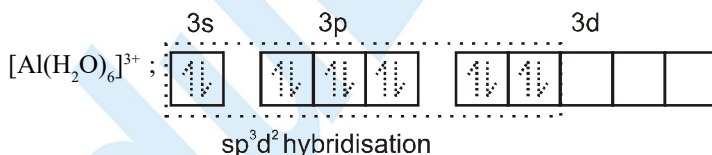
12. Both Statement-1 and Statement-2 are true but Statement-2 is not true explanation (directly not but indirectly true) of Statement-1.

Atomic size of carbon is smaller and thus it has effective overlapping with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are  $C=C$ ,  $C\equiv C$ ,  $C=O$ ,  $C=S$  and  $C\equiv N$ . Heavier elements do not form  $p\pi-p\pi$  bonds because their atomic orbital are too large and diffuse to have effective overlapping.

13. Elemental nitrogen exists as a diatomic molecule because nitrogen can form  $p\pi-p\pi$  multiple bonds which is not possible in case of phosphorus due to repulsion between non-bonded electrons of the inner core. There is no such repulsion in case of smaller nitrogen atoms as they have only  $1s^2$  electrons in their inner core.



19. Both are correct and Statement-2 is the correct explanation of Statement-1. In  $[Al(H_2O)_6]^{3+}$ , aluminium is in +3 oxidation state. So,

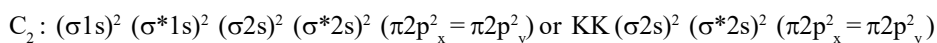


21. Both statements are true and the Statement-2 is the true explanation of Statement-1.

**Fullerenes :** It contains twenty 'six-membered rings' and twelve 'five membered rings'. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo  $sp^2$  hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon atom is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C-C distance of 143.5 pm and 138.3 pm respectively.

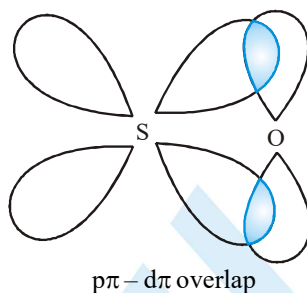
22. Order of acidic character is  $\text{HClO} > \text{HBrO} > \text{HIO}$  as the order of the stability of their conjugate base is  $\text{ClO}^- > \text{BrO}^- > \text{IO}^-$ ; because Cl being small size atom can form effective  $\pi$ -bond with oxygen.

24. Both are true statements and the Statement-2 in the correct explanation of Statement-1.



The bond order of  $\text{C}_2$  is  $1/2 (8 - 4) = 2$  and  $\text{C}_2$  should be diamagnetic. It is important to note that double bond in  $\text{C}_2$  consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond.

27. Both the statements are true and the Statement-2 is the correct answer for the Statement-1.

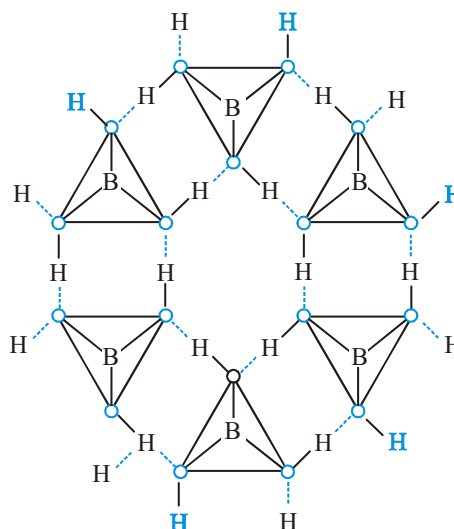


28.  $(\text{CH}_3)_2\ddot{\text{O}}: + \text{B}(\text{CH}_3)_3 \longrightarrow (\text{CH}_3)_2\ddot{\text{O}}: \longrightarrow \text{B}(\text{CH}_3)_3$   
In  $\text{H}_3\text{Si}-\text{O}-\text{H}_3\text{Si}$ , due to  $p\pi-d\pi$  delocalisation, availability of lone pairs on O-atom is decreased and thus disilyl ether does not react with  $\text{B}(\text{CH}_3)_3$ .

29. LiBr has more solubility being more ionic than LiI. Lattice energy as well as hydration energy of LiBr are more than for LiI due to small size of  $\text{Br}^-$ .

30. Due to poor shielding by d-electrons in  $\text{Ga}^{3+}$ , its  $Z_{\text{eff}}$  is more. So its polarising power is more and hence it forms compound with higher covalent character.

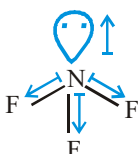
31. In the solid state, the  $\text{B}(\text{OH})_3$  units are hydrogen bonded together in to two dimensional sheets with almost hexagonal symmetry. The layers are quite a large distance apart (3.18 Å) and thus the crystal breaks quite easily into very fine particles.



32.  $\text{NaHCO}_3$ ;   
 $\text{KHCO}_3$ ;  $\left[ \text{O}-\text{C} \begin{array}{l} \diagup \text{O}-\text{H} \diagdown \text{O} \\ \diagdown \text{O} \diagup \text{H}-\text{O} \diagdown \text{O} \end{array} \right]^{2-}$

33. London dispersion force exists among the non-polar molecules like  $F_2$ ,  $O_2$ ,  $I_2$ ,  $Cl_2$  etc. in solid or liquid states. Even in atoms in molecules which have no permanent dipole, instantaneous dipoles will arise as a result of momentary imbalances in electron distribution.

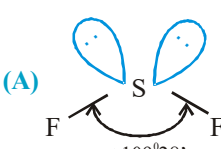
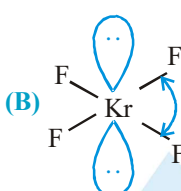
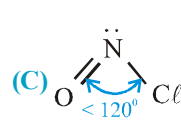
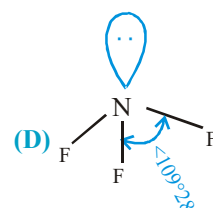
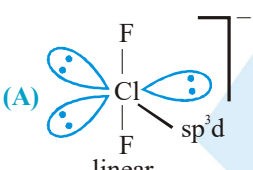
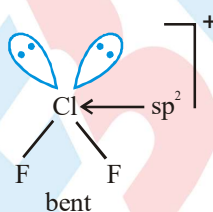
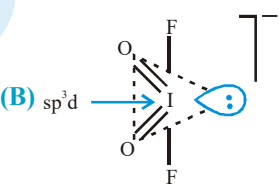
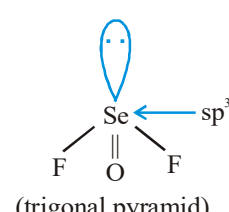
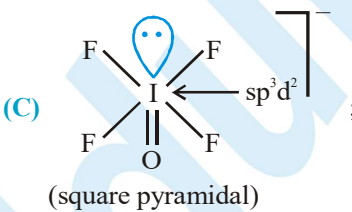
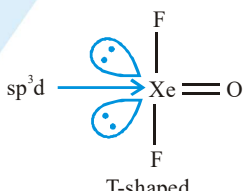
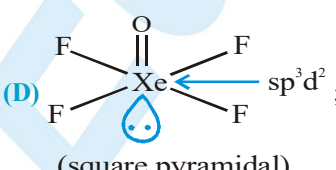
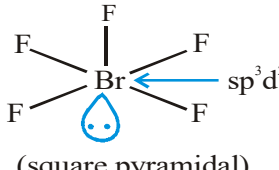
London forces are extremely short range in action and the weakest of all attractive forces. The London forces increase rapidly with molecular weight, or more properly, with the molecular volume and the number of polarizable electrons.

35.  Bond dipoles of N—F bonds are counter balanced to some extent by the dipole moment of lone pair of electron acting in opposite direction. This reduces both the dipole moment and its donor powers.

38. Within the  $Ca^{2+} / SO_4^{2-}$  layers the ions are held together by strong electrovalent bonds. But these separated  $Ca^{2+} / SO_4^{2-}$  layers are linked by relative weak H – bond. The weaker H – bonds link  $SO_4^{2-}$  ions in the intermediate region. Consequently, the gypsum can be readily cleaved and stretched along the layer of water molecules. Anhydride has a completely ionic structure involving only  $Ca^{2+}$  and  $SO_4^{2-}$  ions.

### EXERCISE - 3

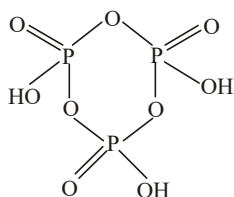
#### Part # I : Matrix Match Type

2. (A)  (B)  (C)  (D) 
3. (A)  ;  (B)  ; 
- (C)  ; 
- (D)  ; 

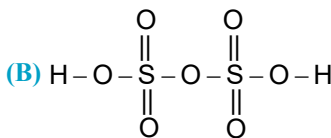


5.

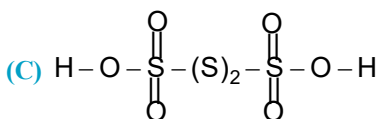
(A)



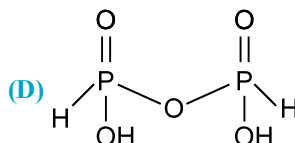
(B)



(C)



(D)



6.

(A)  $N_2^+$ :  $BO = 2.5$  (4 electron in antibonding MO) 1 unpaired electron (Paramagnetic)

$N_2^-$ :  $BO = 2.5$  (5 electron in antibonding MO) 1 unpaired electron (Paramagnetic)

(B)  $NO$ :  $BO = 2.5$  (5 electron in antibonding MO) 1 unpaired electron (Paramagnetic). Last electron in antibonding MO. So, easily removed.

$N_2$ :  $BO = 3$  (4 electron in antibonding MO) 0 unpaired electron (diamagnetic). Last electron in bonding MO. So, not easily removed.

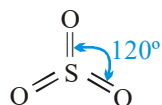
(C)  $NO^+$ :  $BO = 3$  (0 unpaired electron) diamagnetic [ $BO \uparrow \Rightarrow BL \downarrow$ ].

(D)  $He_2^+$ :  $BO = 0.5$  (1 unpaired electron) paramagnetic [1 electron in antibonding MO].

$H_2^+$ :  $BO = 0.5$  (1 unpaired electron) paramagnetic [0 electron in antibonding MO].

9.

(A)

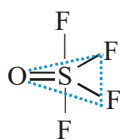


→ non-polar,  $p\pi-d\pi$  bonds present.

All S-O bonds are identical.

No lone pair.

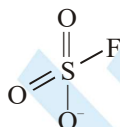
(B)



polar,  $p\pi-d\pi$  bonds present.

No lone pair.

(C)



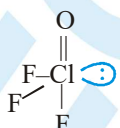
→ polar

→  $p\pi-d\pi$  bonds present.

→ Due to resonance identical

S-O bond length

(D)

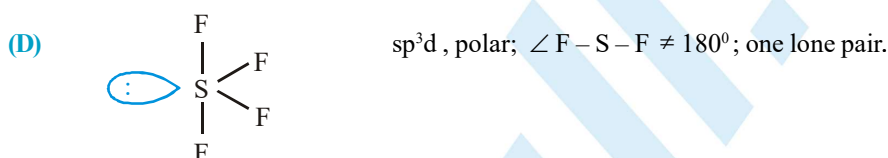
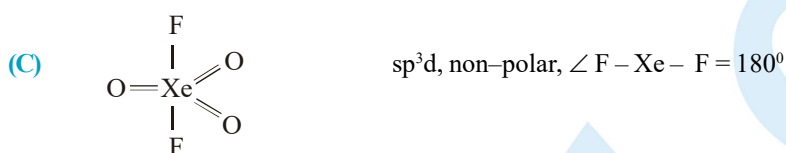
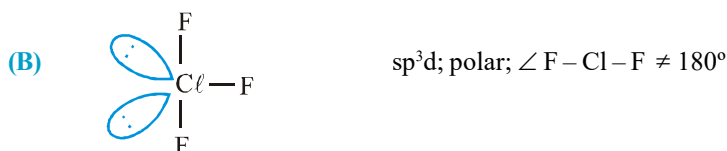
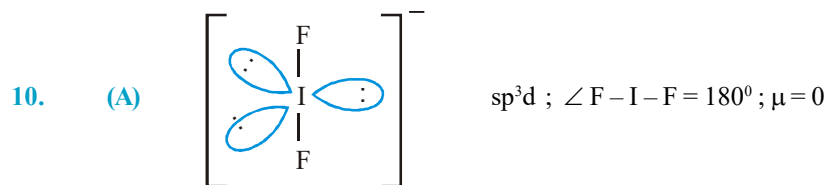


→ polar

→  $p\pi-d\pi$  bonds present.

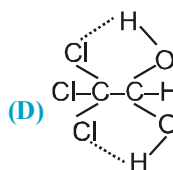
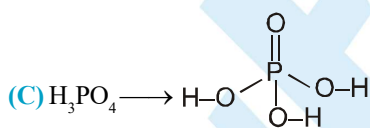
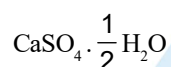
→ lone pair present.





11. (A)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   $\text{SO}_4^{2-}$  is resonance stabilized.

(B)  $\text{Ca}^{2+} / \text{SO}_4^{2-}$  are held together by electrostatic force of attraction i.e., ionic bond but alternate layers by H-bonds with water molecules.



12. (A)  $\text{Br}_2$  is non-polar in nature. All molecules experience London dispersion forces which results from the motion of electrons.

(B) HF has hydrogen bonding in liquid as well as in solid state. HF molecules also experience dispersion forces.

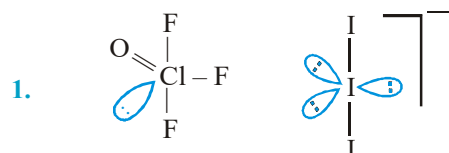
(C) Ion-dipole forces are found in the solutions of ionic compounds in polar solvent where solvated species such as  $\text{Na}(\text{OH}_2)_x^+$  and  $\text{F}(\text{H}_2\text{O})_y^-$  exist. Hydrogen bond exist between water molecules. In addition they also experience dispersion London forces.

(D)  $\text{CH}_3\text{NH}_2$  is a polar molecule that can form hydrogen bonds. In addition, it has dispersion forces.

(E) Induced dipole-dipole interaction exists between non-polar molecules and polar molecules such as clathrate compound of Xe gas with water, when water is frozen under a high pressure of the gas. They have formulae approximating to  $6\text{H}_2\text{O} : 1$  gas atom (i.e.  $\text{Xe} \cdot 6\text{H}_2\text{O}$ ).

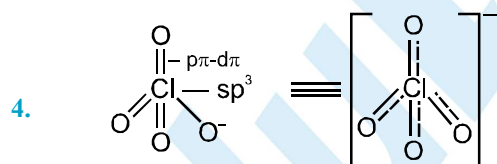
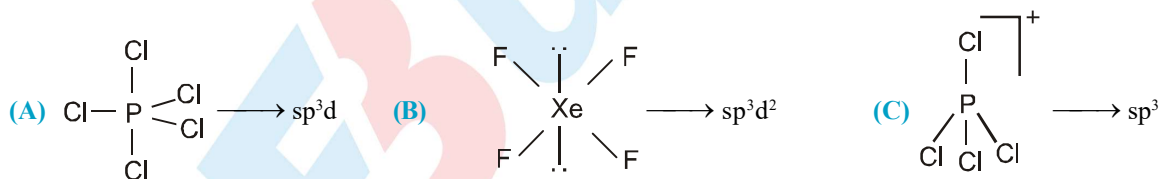
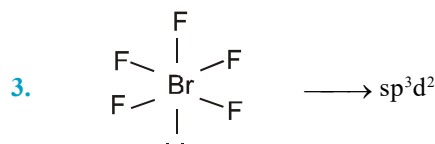
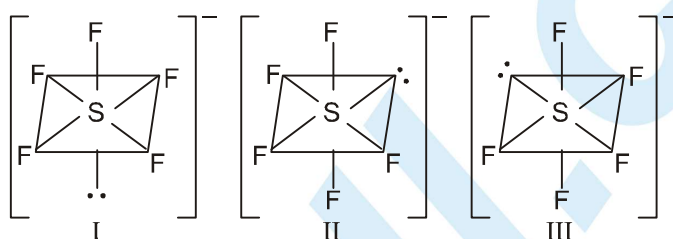
In addition,  $\text{Xe} \cdot 6\text{H}_2\text{O}$  has H-bonding and dispersion forces.

## Comprehension # 1 :

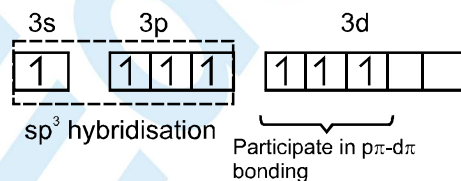


Cl-atom is in  $sp^3d$  hybridisation state. Hence geometry is trigonal bi-pyramidal which is similar to  $I_3^-$

2. Number of electrons pairs = 6 ; number of bond pairs = 5 ; number of lone pairs = 1. According to VSEPR theory geometry of the molecule is square bipyramidal. As all positions are equivalent the lone pair of electrons can occupy any position in octahedral geometry as given below.



Valence shell electron configuration of Cl,  $3s^2 3p^5$



To obtain effective  $p\pi - d\pi$  overlap the size of the d orbital must be similar to size of the p orbital. Hence in chlorine,  $p\pi - d\pi$  bonding is so strong that no polymerization of oxoanions occurs.

5. (A) With hydrogen sulphur does not undergo  $sp^3d^2$  hybridisation because of larger difference in energies between s, p and d-orbitals. Sulphur show +6 oxidation state with highly electronegative elements like O and F.  
 (B) As fluorine is smaller and more electronegative than oxygen.  
 (C) I being large in size, cannot get accommodated around S.

Comprehension # 2 :

1. (A)		Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons /Magnetic property
	$O_2^+$ (dioxygenyl)	2.5	112.3	1 (paramagnetic)
	$O_2$ (dioxygen)	2.0	120.07	2 (paramagnetic)
	$O_2^-$ (superoxide)	1.5	128	1 (paramagnetic)
	$O_2^{2-}$ (peroxide)	1.0	149	0 (diamagnetic)

Bond order  $\propto$  stability (i.e., bond strength)

(B) Helium molecule ( $He_2$ ) :  $(\sigma 1s)^2 (\sigma^* 1s)^2$

Bond order of  $He_2$  is  $\frac{1}{2}(2 - 2) = 0$

The molecular orbital description of  $He_2$  predicts two electrons in a bonding orbital and two electrons in an antibonding orbital, with a bond order of zero - in other words, no bond. The noble gas He has not significant tendency to form diatomic molecules and, like the other noble gases, exists in the form of free atoms.

(C) Carbon molecule ( $C_2$ ) :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$  or KK  $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$

Lithium molecule ( $Li_2$ ) :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$

Peroxide ( $O_2^{2-}$ ) :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$

As all electrons are paired so  $C_2$ ,  $Li_2$  and  $O_2^{2-}$  are diamagnetic.

(D) Fluorine molecule ( $F_2$ ) :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$

3. (B) Oxygen molecule ( $O_2$ ) :  $O_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$

Bond order =  $\frac{1}{2}(10 - 6) = 2.0$ ,

$O_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$

Bond order =  $\frac{1}{2}(10 - 5) = 2.5$ .

Nitrogen molecule ( $N_2$ ) :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$

The bond order of  $N_2$  is  $\frac{1}{2}(10 - 4) = 3$ .

$N^{2+} : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^1$

Bond order =  $\frac{1}{2}(9 - 4) = 2.5$ .

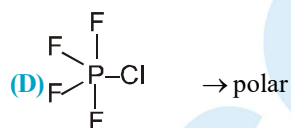
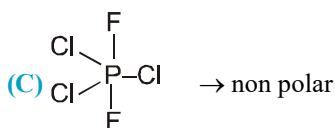
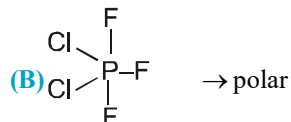
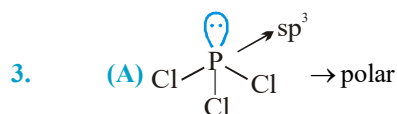
Comprehension # 3 :

1. (D) For more covalent character, small cation and large anion are favourable factors. In  $MgS$ ,  $Mg^{2+}$  will have higher polarising power and  $S^{2-}$  will have higher polarisability. Hence there will be higher polarisation of anion resulting in higher covalent character.
2. Due to smaller size of  $Be^{2+}$  and largest size of  $I^-$  amongst all anions i.e.  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$ , there will be greater polarisation of anion. Thus  $BeI_2$  will be most covalent i.e. least ionic.
3. As the size of the cations increases in the order  
 $Si^{4+} < Sn^{4+} < Sn^{2+}$   
 and for size of anions  
 $F^- < Cl^-$   
 so the order of increasing ionic character is  $SiCl_4 < SnCl_4 < SnF_4 < SnCl_2 < SnF_2$ .

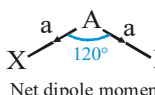
4. As polarizability of anion increases covalent character increases.

**Comprehension # 4 :**

2. Vector addition of dipole moment cancels the dipole moment due to three C-Cl bonds. Only one remains.



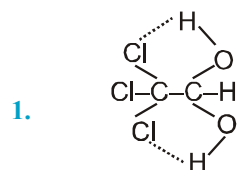
**Comprehension # 5 :**

1.   

$$\text{Net dipole moment} = \sqrt{a^2 + a^2 + 2a \cdot a \cos 120^\circ}$$

$$= \sqrt{2a^2 - a^2} = a$$

**Comprehension # 6 :**



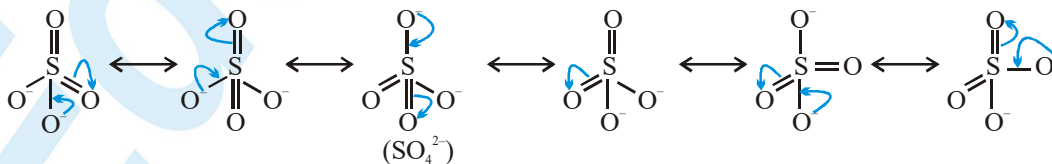
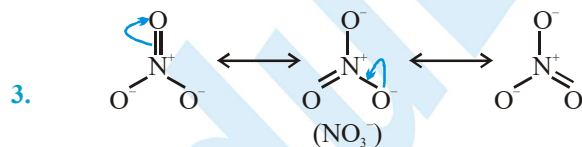
2. o-nitrophenol has intramolecular H-bonding so it will be vaporised first.  
 3.  $D_2O$  has different physical properties than  $H_2O$  max. density of  $D_2O$  is at approximately  $10^\circ C$ .

**EXERCISE - 4**

**Subjective Type**

1. (a) Ionic (b) covalent.

2.  $\angle O-S-O > \angle O-O-O$ .

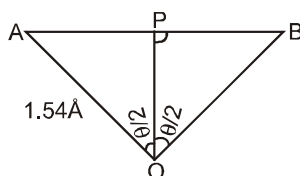


4.  $sp^3 - s$

5. 

6	4	1	5
---	---	---	---

7. Two terminal carbons can be assumed to be at A and B, while the central carbon at O. Then,  $AB = 2AP$



$$\text{But } \frac{AP}{AO} = \sin\left(\frac{\theta}{2}\right)$$

$$= \sin\left(\frac{109^\circ 28'}{2}\right) \quad \therefore \quad (\text{in tetrahedral structure } \theta = 109^\circ 28')$$

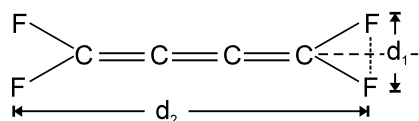
$$= \sin(54^\circ 44')$$

$$\therefore AP = AO \sin(54^\circ 44') = 1.54 \times 0.82 = 1.26 \text{ \AA}$$

$$\therefore AB = 2AP = 2.52 \text{ \AA}$$

**Ans.** 2.52 Å

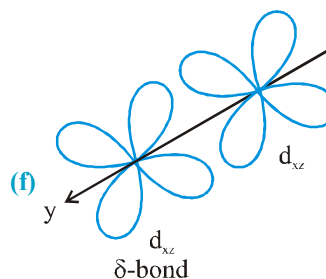
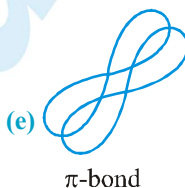
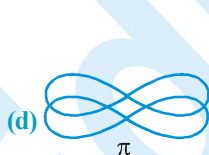
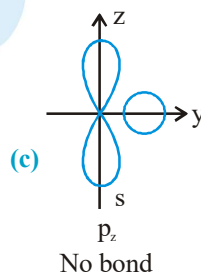
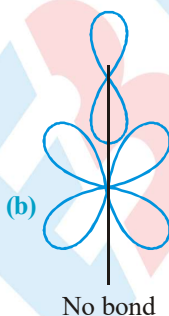
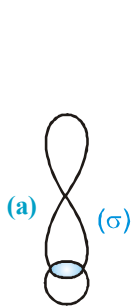
8.



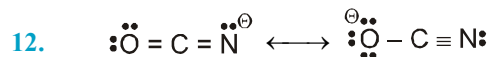
$$d_1 = 2 \times 134 \times \sin 60^\circ \quad \text{pm} = 227.8 \text{ pm} = 228 \text{ pm}$$

$$d_2 = 134 \times 3 + 2 \times 134 \cos 60^\circ \text{ pm} = 536 \text{ pm}$$

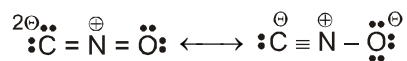
9.



10.  $\text{OF}_4$  and  $\text{OF}_6$  are not possible because oxygen does not have d-orbital for  $\text{sp}^3\text{d}$  and  $\text{sp}^3\text{d}^2$  hybridisation.
11. Because ionic bonds are non directional in nature

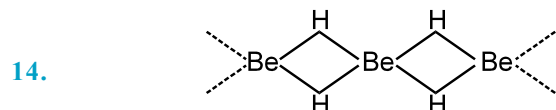


Cyanate ion has canonical structures in which negative charge resides on electronegative O or N.

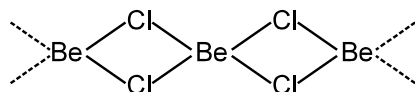


The contributing canonical structures in fulminates are less stable as both contain  $\oplus$  as well as  $\ominus$  charge.

13. In  $\text{BF}_3$ , B is electron deficient whereas in graphite, 'C' has one free electron, which can conduct electricity.



$(\text{BeH}_2)_n$  contains  $2e - 3c$  bonds whereas



$(\text{BeCl}_2)_n$  contain the usual  $2e - 2c$  bonds.

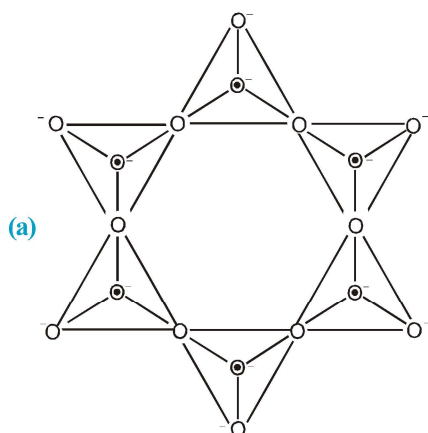
15. (a) 6 (b) 6

16. 634

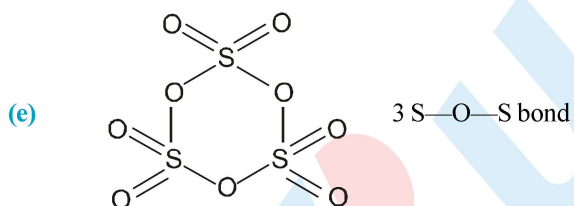
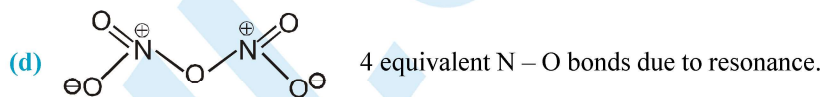
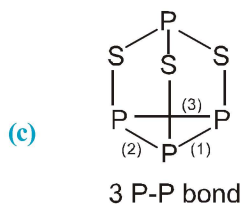
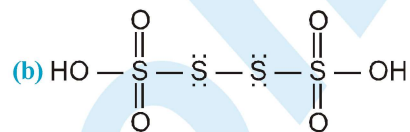
17.

Species	M.O.Configuration	Bond	Magnetic Properties
NO	$\sigma 1s^* 1s \sigma 2s \sigma^* 2s$ $\sigma 2p_x \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \begin{bmatrix} \pi^* 2p_y^1 \\ \pi^* 2p_z^0 \end{bmatrix}$	$\frac{1}{2}[10-5]=2.5$	Paramagnetic
$\text{NO}^+$	$\sigma 1s^* 1s \sigma 2s \sigma^* 2s$ $\sigma 2p_x \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \begin{bmatrix} \pi^* 2p_y^0 \\ \pi^* 2p_z^0 \end{bmatrix}$	$\frac{1}{2}[10-4]=3$	Diamagnetic
$\text{NO}^{2+}$	$\sigma 1s^* 1s \sigma 2s \sigma^* 2s$ $\sigma 2p_x \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^1 \end{bmatrix} \begin{bmatrix} \pi^* 2p_y^0 \\ \pi^* 2p_z^0 \end{bmatrix}$	$\frac{1}{2}[9-4]=2.5$	Paramagnetic
$\text{NO}^-$	$\sigma 1s^* 1s \sigma 2s \sigma^* 2s$ $\sigma 2p_x \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix} \begin{bmatrix} \pi^* 2p_y^1 \\ \pi^* 2p_z^1 \end{bmatrix}$	$\frac{1}{2}[10-6]=2$	Paramagnetic

18

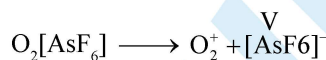


6 shared 'O' atoms.

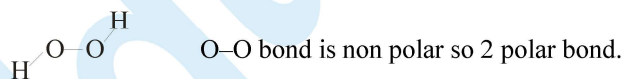


a	b	c	d	e
6	3	3	4	3

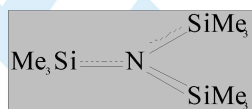
20



$\text{O}_2^{2-} + \text{peroxide ion B.O} = \frac{1}{2}(10 - 8) = 1$

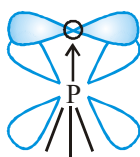
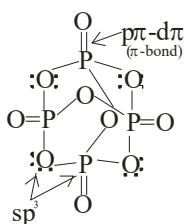


carbon suboxide is  $\text{C}_3\text{O}_2$



Number of l.p is present in  $\text{N}(\text{SiMe}_3)_2$  is zero.

21



The P–O bond lengths shows that the bridging bonds on the edges are 1.60 Å but the P=O bonds on the corners are 1.43 Å and this P=O is formed by  $p\pi-d\pi$  back bonding. A full p-orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is  $127^\circ$  and there is no P–P bonds.

- (i) P = O have bond length of 1.43 Å (8 covalent bonds)
- (ii) P – O have bond length of 1.60 Å (12 covalent bonds)
- (iii) Number of P – O – P linkage = 6.
- (iv) Number of lone pair on each phosphorus atom is zero.

4	12	6	0
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(i) (ii) (iii) (iv)

22.

2n

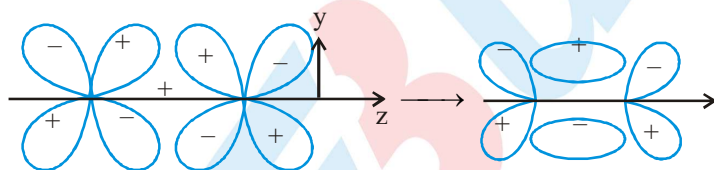
23.

The lone pair of electrons on N atom in trisilyl amine undergoes  $p\pi-d\pi$  delocalisation. Thus this lone pair of electron is not easily available for the donation. On the other hand, in trimethyl amine it is easily available for donation as carbon does not have d-orbital for  $p\pi-d\pi$  delocalisation.

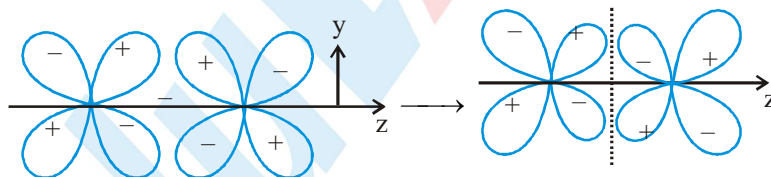
24.

In  $O_2$  and  $N_2$  energy gap between HOMO and LUMO is large so electronic excitation is not possible with visible light. But for halogens, the electronic excitation can be done with visible light because energy difference between HOMO and LUMO is small.

25.

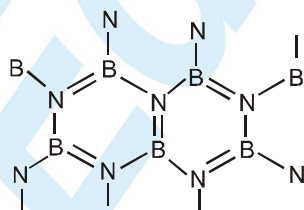


Bonding (3 nodal planes)



Anti bonding (4 nodal planes)

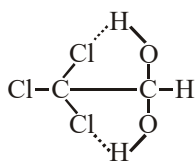
26.



sheet like planar structure.



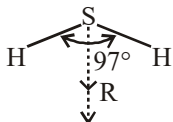
27.  $A \bullet P, CaS, KI, MgO$
28.  $AlCl_3$  shows significant covalent character due to high polarising power of  $Al^{3+}$ . (Fajan's rule) while  $NaCl$  is predominantly ionic. Hence  $NaCl$  has higher M.P. and B.P. against  $AlCl_3$ .
29. Alkali metals have one loosely bound electron which can easily be excited by heat. During de-excitation the electron imparts colour to the flame.
30. (i)  $Mg^{2+} < Fe^{2+} < Ni^{2+} < Zn^{2+}$  (ii)  $Al^{3+} < Fe^{3+} < Ga^{3+}$
31. (i)  $XeF_2 > XeF_4 > XeF_6$   
 (ii)  $TiCl_2 > TiCl_3 > TiCl_4$   
 (iii)  $NaCl > MgCl_2 > AlCl_3$
32.  $Al^{3+}$ , As per Fajan's rule, higher the charge on cation, higher will be its polarising power.
33.  $H-C \equiv C-H$   $sp$  Hybridisation.  
 Due to  $sp$  hybridisation of C atom, the electronegativity of C is more and hence can form H-bond with HF.
34. The structure of chloral hydrate is as follows



Its stability is due to intermolecular H-bonding.

35. Thio-ethers have higher boiling points due to their higher molecular weights than that of ethers.
36.  $\Delta EN = 1.4$   
 % ionic character = 29.26  
 $\mu_{\text{observed}} = 1.4 \text{ D} \Rightarrow \mu_{\text{theoretical}} = 4.8 \text{ D} \Rightarrow d = 1 \text{ \AA}$
37. Percentage of IC =  $\frac{6 \times 10^{-18}}{4.8 \times 10^{-10} \times 2.5 \times 10^{-8}} \times 100 = 50\%$
38. Dipole moment of compound would have been completely ionic  
 $= (4.8 \times 10^{-10} \text{ esu})(2.25 \times 10^{-8} \text{ cm}) = 4.8 \times 2.25 \text{ D}$   
 so % ionic character =  $\frac{9}{4.8 \times 2.25} \times 100\% = 83.33\%$

39



$$\mu_R = \sqrt{2\mu_{S-H}^2 + 2\mu_{S-H}^2 \times \cos 97^\circ}$$

$$\mu_R = \sqrt{2} \times \mu_{S-H} \times \sqrt{1-0.12}$$

$$\mu_R = \sqrt{2} \times \mu_{S-H} \times \sqrt{0.88}$$

$$\mu_{S-H} = \frac{1.5}{\sqrt{2} \times 0.94} D$$

$$(\mu_{S-H})_{Cal} = \frac{0.15 \times 10^{-9} \times 1.6 \times 10^{-19}}{\frac{10}{3} \times 10^{-30}}$$

$$(\mu_{S-H})_{Cal} = 3 \times 0.15 \times 1.6 \times 10 D$$

$$\text{So \% Ionic character} = \frac{1.5}{\sqrt{2} \times 0.94} \times \left[ \frac{1}{0.15 \times 16.3} \right] \times 100 = 16\%$$

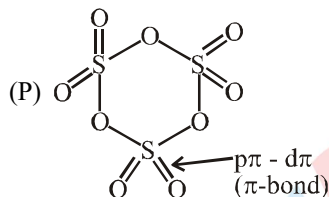
41



42.

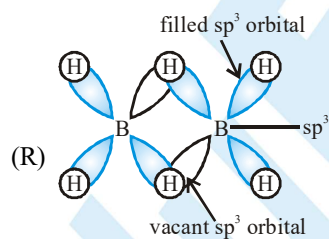
C-F bond is most polar due to maximum difference in electronegativity.

43

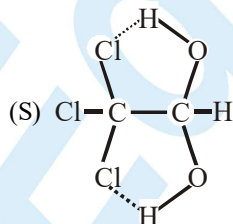


No of  $p\pi-d\pi$  bonds = 6.

(Q)  $\text{NOHSO}_4$  exists as  $\text{NO}^+$  and  $\text{HSO}_4^-$ ;  $\text{NO}^+$  is derivative of oxygen and isoelectronic with  $\text{O}_2^{2+}$ . Bond order is  $1/2(10-4) = 3$ .



No of vacant  $sp^3$  hybrid orbitals participating in the formation of banana bonds are 2.



44. Theoretical value of dipole moment of a 100% ionic character =  $e \times d$

$$= (1.60 \times 10^{-19} \text{ C})(1.41 \times 10^{-10} \text{ m}) = 2.26 \times 10^{-29} \text{ Cm}$$

Observed value of dipole moment =  $2.60 \times 10^{-30} \text{ Cm}$

$$\text{Percent ionic character} = \frac{\text{observed value}}{\text{theoretical value}} \times 100 = \frac{2.60 \times 10^{-30}}{2.26 \times 10^{-29}} \times 100 = 11.5\% \text{ Ans.}$$

45. For a diatomic molecule dipole moment  $\mu = e \times d$

$$\therefore \text{Electronic charge} = \frac{\mu}{d} = \frac{1.2 \times 10^{-18} \text{ esu cm}}{1.0 \times 10^{-8} \text{ cm}}$$

Actual value of electronic charge =  $4.8 \times 10^{-10} \text{ esu}$

$$\therefore \text{Fraction of the electronic charge} = \frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.25$$

46. (i) Bond order of  $\text{N}_2 = 1/2 (10 - 4) = 3$

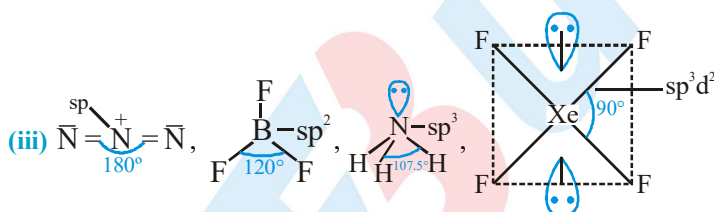
$$\text{Bond order of } \text{O}_2 = 1/2 (10 - 6) = 2$$

$$\text{Bond order of } \text{F}_2 = 1/2 (10 - 8) = 1$$

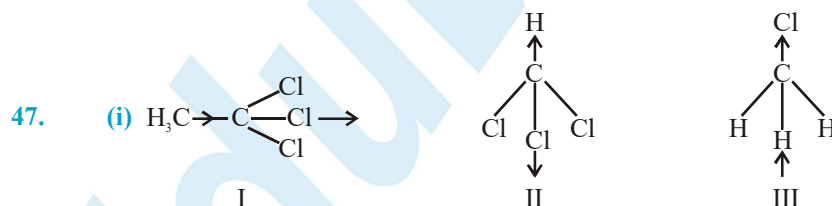
$$\text{Bond order of } \text{O}_2^+ = 1/2 (10 - 5) = 2.5$$

Bond order is directly proportional to the bond strength and so, the increasing order of their bond dissociation energies is :  $\text{F}_2 < \text{O}_2 < \text{O}_2^+ < \text{N}_2$ .

(ii) The strength of H – bond mainly depends on the electronegativity of the atom attached to the H atom and it increases with increasing electronegativity of the atom attached to polar H atom. So the increasing order of strength of hydrogen bonding ( $\text{X} - \text{H} \cdots \text{X}$ ) is :  $\text{S} < \text{Cl} < \text{N} < \text{O} < \text{F}$



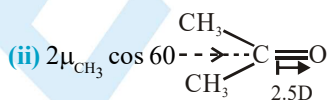
So, the increasing order of bond angles is  $\text{XeF}_4 < \text{NH}_3 < \text{BF}_3 > \text{N}_3^-$



$$\mu_{\text{I}} = 3 \mu_{\text{C-Cl}} \times \cos 70.5^\circ + \mu_{\text{CH}_3} = 1.5 + 0.4 = 1.9 \text{ D}$$

$$\mu_{\text{II}} = 3 \mu_{\text{C-Cl}} \times \cos 70.5^\circ - \mu_{\text{C-H}} = 1.5 - 0.4 = 1.1 \text{ D}$$

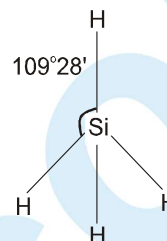
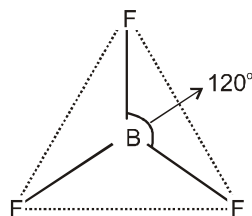
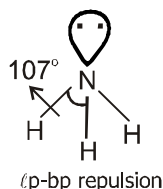
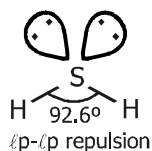
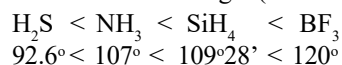
$$\mu_{\text{III}} = 3 \mu_{\text{C-H}} \times \cos 70.5^\circ + \mu_{\text{C-Cl}} = 1.9 \text{ D}$$



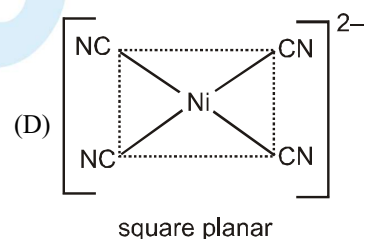
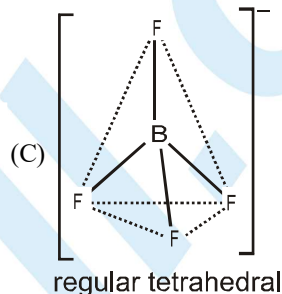
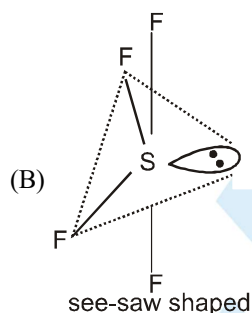
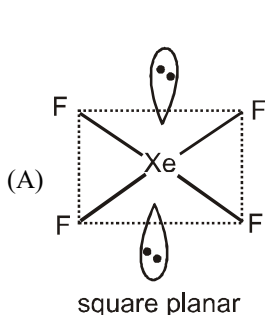
EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

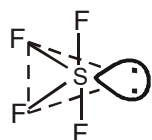
1. The correct order of bond angle (smallest first) is



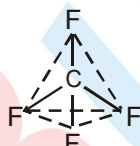
- 4.



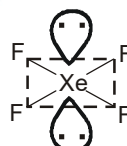
9. According to VSEPR theory



lp = 1  
sp<sup>3</sup> d-hybridisation  
see-saw shape



lp = 0  
sp<sup>3</sup>-hybridisation  
tetrahedral shape

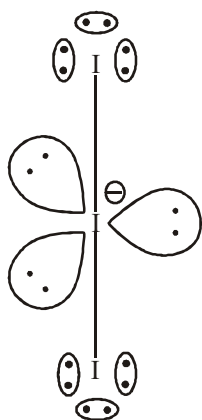


lp = 2  
sp<sup>3</sup>d<sup>2</sup>-hybridisation  
square planar shape

13. The elements of group 14 show an oxidation state of +4 and +2. The compounds showing an oxidation state of +4 forms covalent compound and have tetrahedral structures. e.g.  $\text{SnCl}_4$ ,  $\text{PbCl}_4$ ,  $\text{SiCl}_4$ , etc. whereas those which show +2 oxidation state are ionic in nature and behave as reducing agent. e.g.  $\text{SnCl}_2$ ,  $\text{PbCl}_2$  etc. Further as we move down the group the tendency of the element to form covalent compound decreases but the tendency to form ionic compound increases.
17. Because of highest electronegativity of F, hydrogen bonding in  $\text{F}-\text{H} \cdots \text{F}$  is strongest.
20.  $\text{O}_2^{2-}$  ( $8 + 8 + 2 = 18$ ):  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^2 \pi^* 2p_y^2$ ; all electrons are paired. So diamagnetic.
22. Structure of  $\text{IF}_7$  is pentagonal bipyramidal
24.  $\text{XeF}_2$  has maximum lone pairs out of the given options.  
Number of lone pairs = 3
29.  $\text{PF}_5$  trigonal bipyramidal  
 $\text{BrF}_5$  square pyramidal (distorted)
30. NO is paramagnetic in gaseous state.
33. Xe has highest boiling point because boiling point increases with increase in molecular mass.

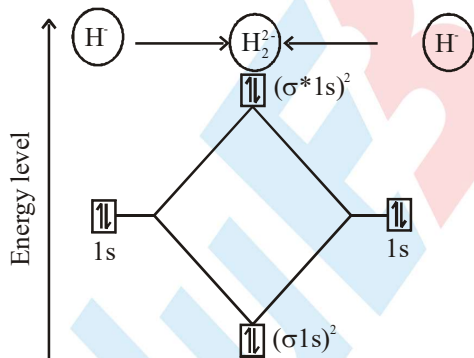
39. NO  $\Rightarrow$  One unpaired electron is present in  $\pi^*$  molecular orbital.  
 CO  $\Rightarrow$  No unpaired electron is present  
 $B_2 \Rightarrow$  Two unpaired electrons are present in  $\pi$  bonding molecular orbitals.  
 $O_2 \Rightarrow$  Two unpaired electrons are present in  $\pi^*$  molecular orbitals.
40. ions  $O^{2-}$   $F^-$   $Na^+$   $Mg^{2+}$   
 Atomic number = 8 9 11 12  
 No. of  $e^-$  = 10 10 10 10  
 therefore  $O^{2-}$ ,  $F^-$ ,  $Na^+$ ,  $Mg^{2+}$  are isoelectronic

41.



Total number of lone pair in  $I_3^-$  is 9.

42. The electronic configuration of  $H_2^{2\ominus}$  is  $\Rightarrow (\sigma 1s^2), (\sigma^* 1s)^2$

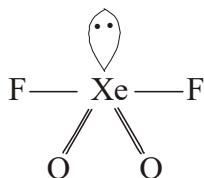


$$\text{Bond order of } H_2^{2\ominus} = \frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0.$$

Hence  $H_2^{2\ominus}$  does not exist, due to zero bond order.

1. Molecular orbital electronic configuration is  $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2 \pi_{2p_x}^2 \pi_{2p_y}^2 \pi_{2p_x}^{*1} \pi_{2p_y}^{*0}$   
As it contains one unpaired electron it is paramagnetic and bond order =  $(10 - 5) / 2 = 2.5$  ( $O_2 = 2.0$ ).

17. Structure of  $XeO_2F_2$  molecule is see saw.

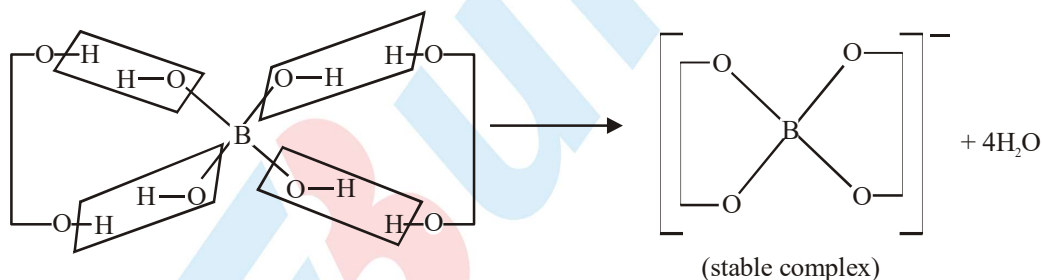


19. (B, D)

(A)  $H_3BO_3$  is a weak monobasic Lewis acid.



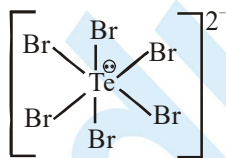
(B) Equilibrium (i) is shifted in forward direction by the addition of syn-diols like ethylene glycol which forms a stable complex with  $B(OH)_4^-$ .



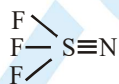
(C) It has a planar sheet like structure due to hydrogen bonding.

(D)  $H_3BO_3$  is a weak electrolyte in water.

34. 6



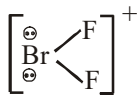
lone pair in C.A. is 1



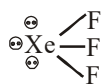
lone pair of electron = 0

lone pair of electron = 3

Total sum is  $0 + 1 + 2 + 3 = 6$



lone pair = 2



35. 5 or 6

Diamagnetic species are



## MOCK TEST

1. (B)

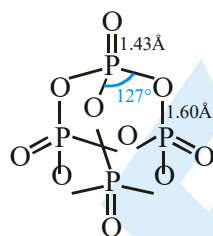
As anion is same, the covalent character in ionic compound will depend upon the size and charge on the cation. According to Fajan's rule,  $\text{PbO}$  (most ionic) =  $\text{Pb}^{2+}$ ,  $\text{Mn}_2\text{O}_7$  (most covalent) =  $\text{Mn}^{+7}$ .

2. (D)

Hybridisation is calculated by steric number rule.  
Steric no. = no. of atoms attached to central atom + no. of lone pairs present on central atom.

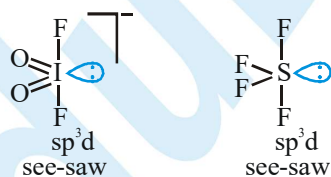
Steric no. for $\text{IO}_4^-$ = 4 + 0 = 4	$\text{sp}^3$ ;
Steric no. for $\text{ICl}_4^-$ = 4 + 2 = 6	$\text{sp}^3\text{d}^2$
Steric no. for $\text{IF}_4^+$ = 4 + 1 = 5	$\text{sp}^3\text{d}$ ;
Steric no. for $\text{SO}_3$ = 3 + 0 = 3	$\text{sp}^2$
Steric no. for $\text{SO}_4^{2-}$ = 4 + 0 = 4	$\text{sp}^3$ ;
Steric no. for $\text{SO}_3^{2-}$ = 3 + 1 = 4	$\text{sp}^3$
Steric no. for $\text{PCl}_4^+$ = 4 + 0 = 4	$\text{sp}^3$ ;
Steric no. for $\text{BF}_4^-$ = 4 + 0 = 4	$\text{sp}^3$
Steric no. for $\text{XeO}_3$ = 3 + 1 = 4	$\text{sp}^3$ ;
Steric no. for $\text{XeO}_4$ = 4 + 0 = 4	$\text{sp}^3$
Steric no. for $\text{XeF}_4$ = 4 + 2 = 6	$\text{sp}^3\text{d}^2$ ;
Steric no. for $\text{ClO}_4^-$ = 4 + 0 = 4	$\text{sp}^3$

3. (A)

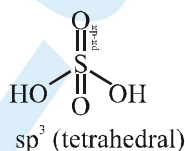
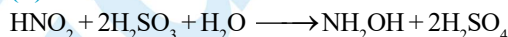


(A) In  $\text{P}_4\text{O}_{10}$ , POP angle is not  $180^\circ$

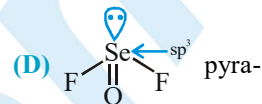
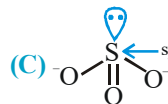
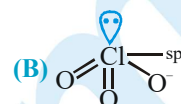
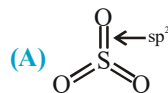
4. (D)



5. (C)



6. (D)



7. (D)

$$\mu = q \times d$$

$$1.2 \times 10^{-18} = q \times 10^{-8} \text{ cm}$$

$$q = \frac{1.2 \times 10^{-18}}{10^{-8}} = 1.2 \times 10^{-10}$$

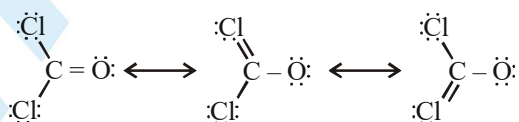
$$\% \text{ charge} = \frac{q}{e} \times 100 = \frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} \times 100 = 25\%$$

8. (D)

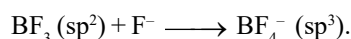
(A) In  $(\text{CH}_3)_3\text{SiOH}$ , because of  $p\pi-d\pi$  deocalisation between silicon and oxygen.  $(\text{CH}_3)_3\text{SiO}^-$  becomes stable.

(B) Si having larger size is unable to form multiple like C in CO and thus  $\text{SiO}_3$  is unstable.

(C) Due to resonance.



9. (A)



10. (D)

(A), (B) M.O. for  $\text{C}_2 =$

$$\sigma_1 s^2 < \sigma_1^* s^2 < \sigma_2 s^2 < \sigma_2^* s^2 < \pi_{2p_x}^2 = \pi_{2p_y}^2 < \sigma_{2p_z} < \sigma_{2p_x}^* < \sigma_{2p_y}^* < \sigma_{2p_z}^*$$

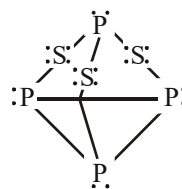
HOMO LUMO

two  $\pi$  molecular orbitals are involved in bonding.

(C) It is isoelectronic with  $\text{N}_2$  and has one sigma and two pi-bonds.

(D) In both, all electrons are paired so diamagnetic.

11. (A, B, C)

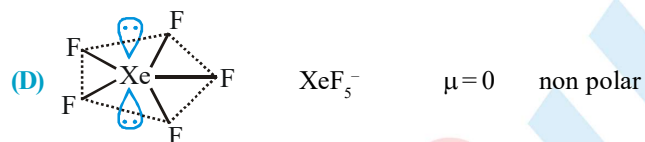
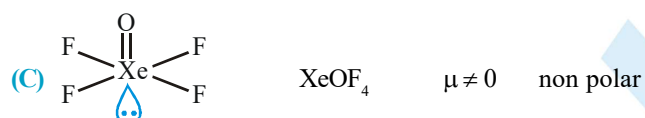
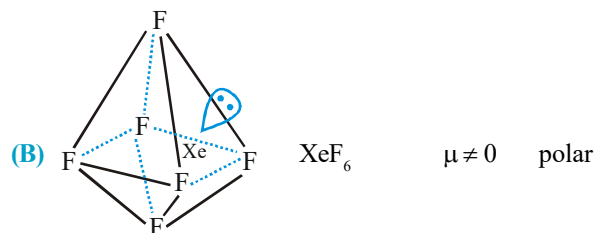
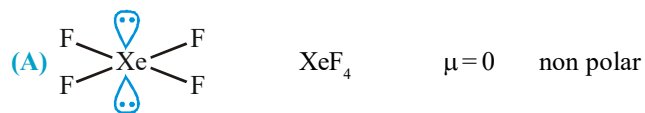




So, number of P — S bonds = 6; number of P—P bonds = 3; total number of lone pairs = 10 and all atoms i.e. P and S have  $sp^3$  hybridisation.

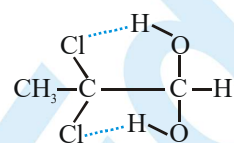
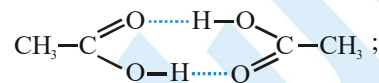
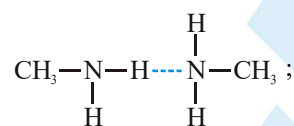
12. (B, C)

Polarity depends on net dipole moment. If dipole moment  $\mu = 0$  it is nonpolar.



13. (A, C, D)

Hydrogen bonding is possible in  $CH_3NH_2$ ,  $CH_3COOH$ ,  $CCl_3CH(OH)_2$



14. (A, B, D)

(A) According to VSEPR theory as electronegativity of central atom decreases, bond angle decreases. So bond angle of  $H_2O > H_2S > H_2Se > H_2Te$

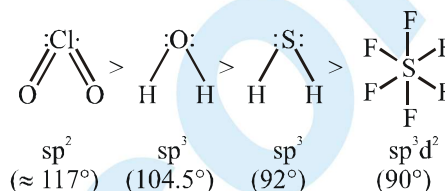
(B)  $C_2H_2 > C_2H_4 > CH_4 > NH_3$ . In  $NH_3$  there is bp-lp repulsion

so bond angle decreases to  $107^\circ$  from  $109.5^\circ$

sp	sp <sup>2</sup>	sp <sup>3</sup>	sp <sup>3</sup>
180°	120°	109.5°	107°

(C)  $SF_6 < NH_3 < H_2O < OF_2$  in this case bond angle of  $NH_3$  is highest because lp-lp repulsion is absent in it.

(D)  $ClO_2 > H_2O > H_2S > SF_6$



**Note :** It is supposed that in  $H_2S$  the hybrid orbitals do not participate in bonding but pure p-atomic orbitals participate in bonding.

15. (A, C)

For  $sp^3d^2$  steric no. is 6

Steric no. of  $IF_5 = 5 + 1 = 6$ ;

Steric no. of  $XeF_4 = 4 + 2 = 6$ ;

Steric no. of  $XeOF_4 = 5 + 1 = 6$ ;

Steric no. of  $ICl_4^- = 4 + 2 = 6$ .

But in  $XeF_4$  &  $ICl_4^-$  dipole moment is zero because of symmetrical molecule and therefore, these are non-polar.

16. (B)

Within the  $Ca^{2+} / SO_4^{2-}$  layers the ions are held together by strong electrovalent bonds. But these separated  $Ca^{2+} / SO_4^{2-}$  layers are linked by relative weak H-bond. The weaker H-bonds link  $SO_4^{2-}$  ions in the intermediate region. Consequently, the gypsum can be readily cleaved and stretched along the layer of water molecules.

Anhydride has a completely ionic structure involving only  $Ca^{2+}$  and  $SO_4^{2-}$  ions.

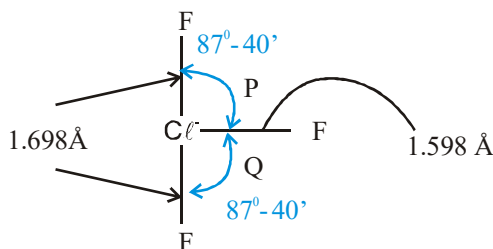
17. (B)

Both S-1 and S-2 are true statements but are different and reason is not true explanation of assertion.

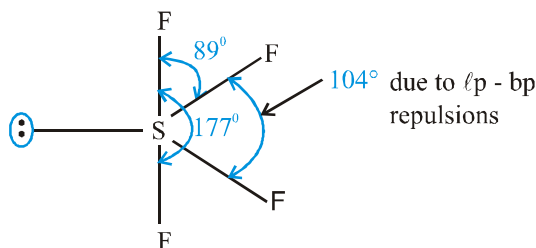
High electronegativity of atoms attached to carbon atom indirectly results into the contraction of the size of p-orbitals. As carbon atomic size is smaller and thus it has effective overlapping.

18. (A)





19. (D)



20. (A)

Transition metal ions have pseudo inert gas configuration which have higher polarising power due to poor shielding of d-electrons. Alkali metal and alkaline earth metal ions have less polarising power due to inert gas configuration (more shielding effect of s- and p-electrons as compared to d-electrons).

21. (A)

As size of cation decreases and charge on cation increases, the polarisation increases according to Fajan's rule. Hence the covalent character increases.

22. (C)

As size of cation increases and charge on cation decreases, the polarisation decreases according to Fajan's rule. Thus the ionic character increases. So SnO with +2 oxidation state will be most ionic.

23. (D)

AgI shows highest polarisation due to following two factors (A)  $\text{Ag}^+$  has pseudo inert gas configuration (B)  $\text{I}^-$  is biggest anion.

24. (D)

(A) Bond order  $\propto \frac{1}{\text{bond length}}$

Bond order  $\text{O}_2^+ = 2.5$ ,  $\text{O}_2 = 2$ ,  $\text{O}_2^- = 1.5$ .  
so correct order of bond length is  $\text{O}_2^- > \text{O}_2 > \text{O}_2^+$ .

(B) Bond order for  $\text{He}_2 = \frac{2-2}{2} = 0$ . So  $\text{He}_2$  does not exist.

(C) In all these molecules all electrons are paired in molecules orbitals. So they are all diamagnetic.

(D)  $\text{F}_2$  MOT configuration.  
 $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^2 \pi^* 2p_z^2$   
 $\sigma^* 2p_z^2$

25. (A)

	$\text{O}_2$	$\text{O}_2^-$	$\text{O}_2^{2-}$	$\text{O}_2^+$
Bond Order	2	1.5	1	2.5

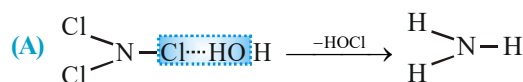
26. (B)

Species	$\text{N}_2$	$\text{N}_2^+$	$\text{O}_2$	$\text{O}_2^+$
Bond Order	3	2.5	2	2.5

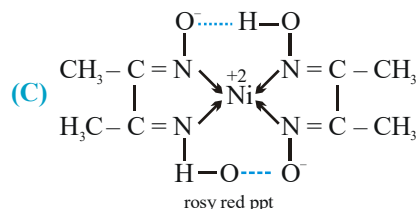
27. (C)

(A), (B) and (D) have intermolecular H-bonding (Y) while anion of Caro's acid (i.e.  $\text{HSO}_5^-$ ) has intramolecular H-bonding (X) as shown below.

28. (C)



(B) Association of molecules leads to a high melting solid because of inter molecular H-bonding (Y).



(D) Ionic peroxides form well crystallised hydrates such as  $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{M}''\text{O}_2 \cdot 8\text{H}_2\text{O}$ . These compounds contain discrete  $\text{O}_2^{2-}$  ions to which water molecules are hydrogen bonded, giving chains of the type shown in structure  $\cdots \text{O}_2^{2-} \cdots (\text{H}_2\text{O})_8 \cdots \text{O}_2^{2-} \cdots (\text{H}_2\text{O})_8 \cdots$ . The formation of such stable hydrates, accounts for the extreme hygroscopic nature of crystalline peroxide.

29. (B)

In the solid state, the  $\text{B}(\text{OH})_3$  units are intermolecular H-bonded together into two dimensional sheets with almost hexagonal symmetry the layers are quite a large distance apart (5.18 Å) and thus crystal break quite easily into very fine particles.