CHAPTER 4

Chemical Bonding and Molecular Structure

1. In which of the following species the interatomic bond angle is 109° 28'? **[2002]**
(a) $NH_3, (BF_4)^{-1}$ (b) $(NH_4)^+, BF_3$
(c) NH_3, BF_4 (d) $(NH_2)^{-1}, BF_3$.

2. Which of the following are arranged in an increasing order of their bond strengths? **[2002]**
(a) $O_2^- < O_2 < O_2^+ < O_2^{2-}$
(b) $O_2^{2-} < O_2^- < O_2 < O_2^+$
(c) $O_2^- < O_2^{2-} < O_2 < O_2^+$
(d) $O_2^+ < O_2 < O_2^- < O_2^{2-}$

3. Hybridisation of the underline atom changes in: **[2002]**
(a) $\underline{Al}H_3$ changes to AlH_4^-
(b) $H_2\underline{O}$ changes to H_3O^+
(c) $\underline{N}H_3$ changes to NH_4^+
(d) in all cases

4. An ether is more volatile than an alcohol having the same molecular formula. This is due to **[2003]**
(a) alcohols having resonance structures
(b) inter-molecular hydrogen bonding in ethers
(c) inter-molecular hydrogen bonding in alcohols
(d) dipolar character of ethers

5. Which one of the following pairs of molecules will have permanent dipole moments for both members? **[2003]**
(a) NO_2 and CO_2 (b) NO_2 and O_3
(c) SiF_4 and CO_2 (d) SiF_4 and NO_2

6. Which one of the following compounds has the smallest bond angle in its molecule? **[2003]**
(a) OH_2 (b) SH_2
(c) NH_3 (d) SO_2

7. The pair of species having identical shapes for molecules of both species is **[2003]**
(a) XeF_2, CO_2 (b) BF_3, PCl_3
(c) PF_5, IF_5 (d) CF_4, SF_4

8. The correct order of bond angles (smallest first) in H_2S, NH_3, BF_3 and SiH_4 is **[2004]**
(a) $H_2S < NH_3 < SiH_4 < BF_3$
(b) $NH_3 < H_2S < SiH_4 < BF_3$
(c) $H_2S < SiH_4 < NH_3 < BF_3$
(d) $H_2S < NH_3 < BF_3 < SiH_4$

9. The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for these two species ? **[2004]**
(a) Bond length in NO^+ is equal to that in NO
(b) Bond length in NO is greater than in NO^+
(c) Bond length in NO^+ is greater than in NO
(d) Bond length is unpredictable

10. The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are respectively **[2004]**
(a) sp^3 and sp^2 (b) sp^2 and sp^3
(c) sp^2 and sp^2 (d) sp^3 and sp^3

11. Which one of the following has the regular tetrahedral structure ? **[2004]**
(a) BF_4^- (b) SF_4
(c) XeF_4 (d) $[Ni(CN)_4]^{2-}$
(Atomic nos. : B = 5, S = 16, Ni = 28, Xe = 54)

12. The maximum number of 90° angles between bond pair-bond pair of electrons is observed in **[2004]**
(a) dsp^2 hybridization
(b) sp^3d hybridization
(c) dsp^3 hybridization
(d) sp^3d^2 hybridization

13. Lattice energy of an ionic compound depends upon **[2005]**
(a) Charge on the ion and size of the ion
(b) Packing of ions only
(c) Size of the ion only
(d) Charge on the ion only

14. Which of the following molecules/ions does not contain unpaired electrons? **[2006]**
(a) N_2^+ (b) O_2
(c) O_2^{2-} (d) B_2

15. In which of the following molecules/ions are all the bonds **not** equal? **[2006]**
(a) XeF_4 (b) BF_4^-
(c) SF_4 (d) SiF_4

16. The decreasing values of bond angles from NH_3 (106°) to SbH_3 (101°) down group-15 of the periodic table is due to **[2006]**
(a) decreasing lp-bp repulsion
(b) decreasing electronegativity
(c) increasing bp-bp repulsion
(d) increasing p-orbital character in sp^3

17. Which of the following species exhibits the diamagnetic behaviour? **[2007]**
(a) NO (b) O_2^{2-}
(c) O_2^+ (d) O_2.

18. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}? **[2007]**
(a) $Ca^{2+} < Mg^{2+} < Be^+ < K^+$
(b) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(c) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$.

19. In which of the following ionization processes, the bond order has increased and the magnetic behaviour has changed? **[2007]**
(a) $N_2 \rightarrow N_2^+$ (b) $C_2 \rightarrow C_2^+$
(c) $NO \rightarrow NO^+$ (d) $O_2 \rightarrow O_2^+$.

20. Which of the following hydrogen bonds is the strongest? **[2007]**
(a) O – H - - - F (b) O – H - - - H
(c) F – H - - - F (d) O – H - - - O.

21. Which one of the following pairs of species have the same bond order? **[2008]**
(a) CN^- and NO^+ (b) CN^- and CN^+
(c) O^-_2 and CN^- (d) NO^+ and CN^+

22. The bond dissociation energy of B – F in BF_3 is 646 kJ mol^{-1} whereas that of C – F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B – F bond dissociation energy as compared to that of C – F is **[2008]**
(a) stronger σ bond between B and F in BF_3 as compared to that between C and F in CF_4.
(b) significant pπ – pπ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4.
(c) lower degree of pπ – pπ interaction between B and F in BF_3 than that between C and F in CF_4.
(d) smaller size of B– atom as compared to that of C– atom.

23. Using MO theory, predict which of the following species has the shortest bond length? **[2008]**
(a) O_2^+ (b) O_2^-
(c) O_2^{2-} (d) O_2^{2+}

24. The number of types of bonds between two carbon atoms in calcium carbide is : **[2011RS]**
(a) One sigma, One pi (b) Two sigma, one pi
(c) Two sigma, two pi (d) One sigma, two pi

25. Ortho-Nitrophenol is less soluble in water than *p*- and *m*- Nitrophenols because : **[2012]**
(a) *o*-Nitrophenol is more volatile steam than those of *m*- and *p*-isomers.
(b) *o*-Nitrophenol shows intramolecular H-bonding
(c) *o*-Nitrophenol shows intermolecular H-bonding
(d) Melting point of *o*-Nitrophenol is lower than those of *m*- and *p*-isomers.

26. In which of the following pairs the two species are not isostructural ? **[2012]**
(a) CO_3^{2-} and NO_3^- (b) PCl_4^+ and $SiCl_4$
(c) PF_5 and BrF_5 (d) AlF_6^{3-} and SF_6

27. Which one of the following molecules is expected to exhibit diamagnetic behaviour ? **[2013]**

(a) C_2 (b) N_2
(c) O_2 (d) S_2

28. Which of the following is the wrong statement **[2013]**
(a) ONCl and ONO^- are not isoelectronic.
(b) O_3 molecule is bent
(c) Ozone is violet-black in solid state
(d) Ozone is diamagnetic gas.

29. In which of the following pairs of molecules/ ions, both the species are not likely to exist ? **[2013]**
(a) H_2^+, He_2^{2-} (b) H_2^-, He_2^{2-}
(c) H_2^{2+}, He_2 (d) H_2^-, He_2^{2+}

30. Which one of the following properties is **not** shown by NO? **[2014]**
(a) It is diamagnetic in gaseous state
(b) It is neutral oxide
(c) It combines with oxygen to form nitrogen dioxide
(d) It's bond order is 2.5

31. The species in which the N atom is in a state of *sp* hybridization is : **[JEE M 2016]**
(a) NO_3^- (b) NO_2
(c) NO_2^+ (d) NO_2^-

32. Which of the following species is not paramagnetic ? **[JEE M 2017]**
(a) NO (b) CO
(c) O_2 (d) B_2

Answer Key

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(a)	(b)	(a)	(c)	(b)	(b)	(a)	(a)	(b)	(b)	(a)	(d)	(a)	(c)	(d)
16	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
(b)	(b)	(d)	(c)	(c)	(a)	(b)	(d)	(d)	(b)	(c)	(a, b)	()	(c)	(a)
31	**32**													
(c)	(b)													

SOLUTIONS

1. **(a)** In NH_3 and BF_4^- the hybridisation is sp^3 and the bond angle is almost 109° 28'.

2. **(b)** $O_2^+(15) = KK\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$
$\{\pi 2p_y^2 = \pi 2p_z^2, \{\pi^* 2p_y^1 = \pi 2p_z^0$

$$\text{Bond order} = \frac{1}{2}(8-3) = \frac{5}{2} = 2.5$$

$O_2(16) = KK\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$
$\{\pi 2p_y^2 = \pi 2p_z^2, \{\pi^* 2p_y^1 = \pi^* 2p_z^1$

$$\text{Bond order} = \frac{1}{2}(8-4) = 2$$

$O_2^-(17) = KK\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$
$\{\pi 2p_y^2 = \pi 2p_z^2, \{\pi^* 2p_y^2 = \pi^* 2p_z^1$

$$\text{Bond order} = \frac{1}{2}(8-5) = 1.5$$

$O_2^{2-}(18) = KK\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2,$
$\{\pi 2p_y^2 = \pi 2p_z^2, \{\pi^* 2p_y^2 = \pi^* 2p_z^2$

$$\text{Bond order} = \frac{1}{2}(8-6) = 1$$

NOTE As we know that as the bond order decreases, stability also decreases and hence the bond strength also decreases. Hence the correct order of their increasing bond strength is

$$O_2^{2-} < O_2^- < O_2 < O_2^+$$

3. **(a)** **TIPS / Formulae**

$$\text{Hybridisation} = \frac{1}{2}\left[\begin{pmatrix}\text{No. of electrons}\\ \text{in valence}\\ \text{shell of atom}\end{pmatrix} + \begin{pmatrix}\text{No.of monovalent}\\ \text{atoms around it}\end{pmatrix} - \begin{pmatrix}\text{charge on}\\ \text{cation}\end{pmatrix} +\right.$$

$$\begin{pmatrix}\text{charge on}\\ \text{anion}\end{pmatrix}$$

(a) For AlH_3,

$$\text{Hybridisation of Al atom} = \frac{1}{2}[3+3-0+0]$$
$$= 3 = sp^2$$

For AlH_4^-,

$$\text{Hybridisation of Al atom} = \frac{1}{2}[3+4-0+1]$$
$$= 4 = sp^3$$

(b) For H_2O,
Hybridisation of O atom

$$= \frac{1}{2}[6+2-0+0] = 4 = sp^3$$

For H_3O^+, Hybridisation of O atom

$$= \frac{1}{2}[6+3-1+0] = 4 = sp^3$$

(c) For NH_3
Hybridisation of N atom

$$= \frac{1}{2}[5+3-0+0] = 4 = sp^3$$

For NH_4^+, Hybridisation of N atom

$$= \frac{1}{2}[5+4-1+0] = 4 = sp^3$$

Thus hybridisation changes only in option (a).

4. (c) In ether, there is no H-bonding while alcohols have intermolecular H-bonding

5. (b) Both NO_2 and O_3 have angular shape and hence will have net dipole moment.

6. (b) In H_2S, due to low electronegativity of sulphur the L.P. - L. P. repulsion is more than B. P. - B. P. repulsion and hence the bond angle is minimum.

	SO_2	H_2O	H_2S	NH_3
Bond angle	119.5°	104.5°	92.5°	106.5°

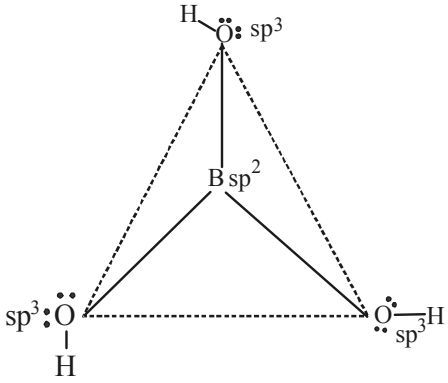
7. (a) Both XeF_2 and CO_2 have a linear structure.
F — Xe — F O = C = O

8. (a) The order of bond angles

$$\underset{120^\circ}{BF_3} > \underset{109^\circ 28'}{SiH_4} > \underset{107^\circ}{NH_3} > \underset{92.5^\circ}{H_2S}$$

9. (b) Now since bond order of NO^+ given (3) is higher than that of NO (2.5). Thus bond length of NO^+ will be shorter.

10. (b)

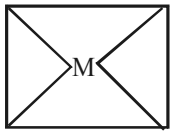


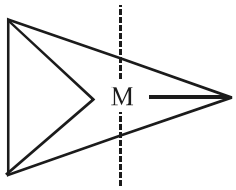
11. (a) XeF_4 (sp^3d^2 square planar),

$[Ni(CN)_4]^{2-}$ (dsp^2 square planar),

BF_4^- (sp^3 tetrahedral), SF_4 (sp^3d see saw shaped)

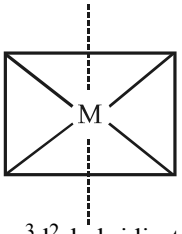
12. (d)





dsp^2 hybridisation — Number of 90° angle between bonds = 4

sp^3d or dsp^3 hybridisation — Number of 90° angle between bonds = 6



sp^3d^2 hybridisation
Number of 90° angle between bonds = 12

13. (a) The value of lattice energy depends on the charges present on the two ions and the distance between them.

14. (c) The distribution of electrons in MOs is as follows :

N_2^+(electrons 13) $\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}\ \pi^2\ \sigma^1\ \pi^*\ \pi^2\ \pi^*\ \sigma^*$

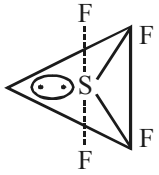
O_2 (electrons 16) $\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}\ \sigma^2\ \pi^2\ \pi^2\ \pi^{*1}\ \pi^{*1}\ \sigma^*$

O_2^{2-} (electrons 18) $\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}\ \sigma^2\ \pi^2\ \pi^2\ \pi^*\ \pi^*\ \sigma^*$

B_2 (electrons 10) $\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}\ \pi^1\ \pi^1$

Only O_2^{2-} does not contain any unpaired electron.

15. (d) In SF_4 the hybridisation is sp^3d and the shape of molecule is



16. (b) The bond angle decreases on moving down the group due to decrease in bond pair-bond pair repulsion.

NH_3	PH_3	ASH_3	SbH_3	BiH_3
107°	94°	92°	91°	90°

NOTE This can also be explained by the fact that as the size of central atom increases sp^3 hybrid orbital becomes more distinct with increasing size of central atom i.e. pure p- orbitals are utilized in M–H bonding

17. (b) Diamagnetic species have no unpaired electrons

$O_2^{2-} \Rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \{\pi 2p_y^2 = \pi 2p_z^2, \{\pi^* 2p_y^2 = \pi^* 2p_z^2$

Whereas paramagnetic species has one or more unpaired electrons as in

$O_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2$,

$\{\pi 2p_y^2 = \pi 2p_z^2,$

$\{\pi^* 2p_y^1 = \pi^* 2p_z^1 - 2$ unpaired electrons

$O_2^+ \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$

$\{\pi 2p_y^2 = \pi 2p_z^2 \{\pi^* 2p_y^1 = \pi^* 2p_z^0 - 1$ unpaired electron

$NO \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$

$\pi 2p_z^2, \{\pi^* 2p_y^1 = \pi^* 2p_z^0 - 1$ unpaired electron

18. (d) Smaller the size and higher the charge more will be polarising power of cation. Since the order of the size of cation is $K^+ > Ca^{++} > Mg^{++} > Be^{++}$. So the correct order of polarising power is $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

19. (c) (a) N_2 : bond order 3, paramagnetic
N_2^- : bond order, 2.5, paramagnetic
(b) C_2 : bond order 2, diamagnetic
C_2^+ : bond order 1.5, paramagnetic
(c) NO : bond order 2.5, paramagnetic
NO^+ : bond order 3, diamagnetic
(d) O_2 : bond order 2, paramagnetic
O_2^+ : bond order 2.5, paramagnetic

20. (c) **NOTE** Greater the difference between electro-negativity of bonded atoms, stronger will be bond. Since F is most electronegative hence F – H ..... F is the strongest bond.

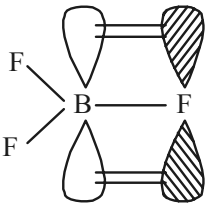
21. (a) For any species to have same bond order we can expect them to have same number of electrons. Calculating the number of electrons in various species.

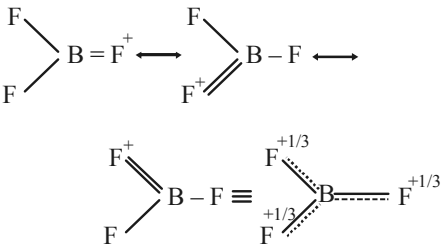
$O_2^-(8+8+1=17)$; $CN^-(6+7+1=14)$

$NO^+(7+8-1=14)$; $CN^+(6+7-1=12)$

We find CN^- and NO^+ both have 14 electrons so they have same bond order. Correct answer is (a).

22. (b) **NOTE** The delocalised $p\pi - p\pi$ bonding between filled *p*-orbital of F and vacant *p*-orbital of B leads to shortening of B–F bond length which results in higher bond dissociation energy of the B–F bond.





23. (d) Bond order

$$= \frac{\text{No. of bonding electrons} - \text{No. of antibonding electrons}}{2}$$

Bond order in $O_2^+ = \frac{10-5}{2} = 2.5$

Bond order in $O_2^- = \frac{10-7}{2} = 1.5$

Bond order in $O_2^{2-} = \frac{10-8}{2} = 1$

Bond order in $O_2^{2+} = \frac{10-4}{2} = 3$

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

$\therefore$ Bond length is shortest in O_2^{2+}.

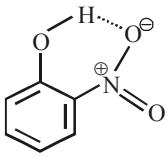
24. (d) Calcium carbide exists as Ca^{2+} and C_2^{2-}. According to the molecular orbital model, C_2^{2-} should have molecular orbital configuration :

$\sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2$

$\{\pi 2p_y^2 = \pi 2p_z^2\}\, \sigma 2p_x^2$

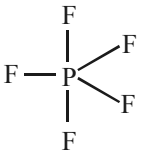
Thus M.O. configuration suggests that it contains one σ & 2π bonds.

25. (b) Compounds involved in chelation become non-polar. Consequently such compounds are soluble in non-polar solvents like ether, benzene etc. and are only sparingly soluble in water whereas meta and para isomers are more soluble in water & less soluble in non-polar solvents.

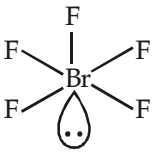


intra-molecular H-bonding

26. (c) PF_5 trigonal bipyramidal



BrF_5 square pyramidal (distorted)



27. (a, b) The molecular orbital structures of C_2 and N_2 are

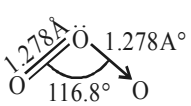
$$N_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2$$

$$C_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2 \pi 2py^2 \pi 2P_z^2$$

Both N_2 and C_2 have paired electrons, hence they are diamagnetic.

28. All options are correct,

(a) $ONCl = 8+7+17 = 32e^-$, $ONO^- = 8+7+8+1 = 24e^-$ } not isoelectronic

(b) 

The central atom is sp^2 hybridized with one lone pair.

(c) It is a pale blue gas. At – 249.7°, it forms violet black crystals.

(d) It is diamagnetic in nature due to absence of unpaired electrons.

29. (c) $H_2^{2+} = \sigma 1s^0\, \sigma^* 1s^0$

Bond order for $H_2^{2+} = \frac{1}{2}(0-0) = 0$

$He_2 = \sigma 1s^2 \sigma^* 1s^2$

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

so both H_2^{2+} and He_2 does not exist.

30. (a) Nitric oxide is paramagnetic in the gaseous state because of the presence of one unpaired electron in its outermost shell. The electronic configuration of NO is

$$\sigma_{1s}^2\, \sigma_{1s}^{*2}\, \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2\, \pi_{2p_x}^2 = \pi_{2p_y}^2\, \pi_{2p_x}^{*1}$$

31. (c) Hybridization (H) = [no. of valence electrons of central atom + no. of Monovalent atoms attached to it + (–ve charge if any) – (+ve charge if any)]

NO^+_2 = i.e. sp hybridisation

NO^-_2 = i.e. sp^2 hybridisation

NO^-_3 = i.e. sp^2 hybridisation

The lewis structure of NO_2 shows a bent molecular geometry with trigonal planar electron pair geometry hence the hybridization will be sp^2

32. (b)

1. NO → one unpaired electron is present in π* molecular orbit hence paramagnetic.

2. $CO \rightarrow \sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_x}^2, \pi_{2p_y}^2, \sigma 2pz^2$

   no unpaired electron hence diamagnetic.

3. $O_2 \rightarrow \sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_z}^2, \pi_{2p_x}^2, \pi_{2p_y}^2, \pi_{2p_x}^{*1}, \pi_{2p_y}^{*1}$

   two unpaired electron hence paramagnetic.

4. $B_2 \rightarrow \sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_x}^1, \pi_{2p_y}^1$

   B_2 contains two unpaired electrons hence paramagnetic