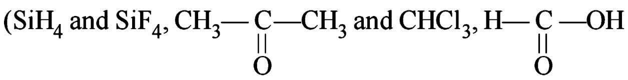
CHAPTER 4

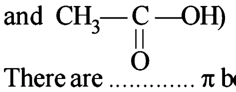
Chemical Bonding and Molecular Structure

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. The angle between two covalent bonds is maximum in .... (CH_4, H_2O, CO_2) *(1981 - 1 Mark)*
2. Pair of molecules which forms strongest intermolecular hydrogen bond is ....


(SiH_4 and SiF_4, $CH_3—\underset{\underset{O}{||}}{C}—CH_3$ and $CHCl_3$, $H—\underset{\underset{O}{||}}{C}—OH$


and $CH_3—\underset{\underset{O}{||}}{C}—OH$) *(1981 - 1 Mark)*

3. There are .... π bonds in a nitrogen molecule. *(1982 - 1 Mark)*
4. .... hybrid orbitals of nitrogen atom are involved in the formation of ammonium ion. *(1982 - 1 Mark)*
5. The shape of $[CH_3]^+$ is .... *(1990 - 1 Mark)*
6. The two types of bonds present in B_2H_6 are covalent and .... *(1994 - 1 Mark)*
7. When N_2 goes to N_2^+, the N–N bond distance ..., and when O_2 goes to O_2^+ the O–O bond distance.... *(1996 - 1 Mark)*

B True / False

1. Linear overlap of two atomic p-orbitals leads to a sigma bond. *(1983 - 1 Mark)*
2. All molecules with polar bonds have dipole moment. *(1985 - ½ Mark)*
3. $SnCl_2$ is a non-linear molecule. *(1985 - ½ Mark)*
4. In benzene, carbon uses all the three p-orbitals for hybridisation. *(1987 - 1 Mark)*
5. sp^2 hybrid orbitals have equal *s* and *p* character. *(1987 - 1 Mark)*
6. The presence of polar bonds in a poly-atomic molecule suggests that the molecule has non-zero dipole moment. *(1990 - 1 Mark)*
7. The dipole moment of CH_3F is greater than that of CH_3Cl. *(1993 - 1 Mark)*

C MCQs with One Correct Answer

1. The compound which contains both ionic and covalent bonds is *(1979)*
   (a) CH_4 (b) H_2 (c) KCN (d) KCl
2. The octet rule is not valid for the molecule *(1979)*
   (a) CO_2 (b) H_2O (c) O_2 (d) CO
3. Element X is strongly electropositive and element Y is strongly electronegative. Both are univalent. The compound formed would be *(1980)*
   (a) X^+Y^- (b) X^-X^+ (c) X–Y (d) X → Y
4. Which of the following compounds are covalent? *(1980)*
   (a) H_2 (b) CaO (c) KCl (d) Na_2S
5. The total number of electrons that take part in forming the bond in N_2 is *(1980)*
   (a) 2 (b) 4 (c) 6 (d) 10
6. Which of the following is soluble in water *(1980)*
   (a) CS_2 (b) C_2H_5OH
   (c) CCl_4 (d) $CHCl_3$
7. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atomic number < 21) are *(1981 - 1 Mark)*
   (a) pure *p* (b) *sp* hybrid
   (c) sp^2 hybrid (d) sp^3 hybrid
8. The ion that is isoelectronic with CO is *(1982 - 1 Mark)*
   (a) CN^- (b) O_2^+ (c) O_2^- (d) N_2^+
9. Among the following, the molecule that is linear is
   (a) CO_2 (b) NO_2 *(1982 - 1 Mark)*
   (c) SO_2 (d) ClO_2
10. The compound with no dipole moment is *(1982 - 1 Mark)*
    (a) methyl chloride (b) carbon tetrachloride
    (c) methylene chloride (d) chloroform
11. Carbon tetrachloride has no net dipole moment because of
    (a) its planar structure *(1983 - 1 Mark)*
    (b) its regular tetrahedral structure
    (c) similar sizes of carbon and chlorine
    (d) similar electron affinities of carbon and chlorine
12. Which one among the following does not have the hydrogen bond? *(1983 - 1 Mark)*
    (a) phenol (b) liquid NH_3
    (c) water (d) liquid HCl
13. The types of bonds present in $CuSO_4.5H_2O$ are only
    (a) electrovalent and covalent *(1983 - 1 Mark)*
    (b) electrovalent and coordinate covalent
    (c) electrovalent, covalent and coordinate covalent
    (d) covalent and coordinate covalent

14. On hybridization of one *s* and one *p* orbitals we get :

(a) two mutually perpendicular orbitals *(1984 - 1 Mark)*

(b) two orbitals at 180°

(c) four orbitals directed tetrahedrally

(d) three orbitals in a plane

15. The molecule having one unpaired electron is : *(1985 - 1 Mark)*

(a) NO (b) CO (c) CN^- (d) O_2

16. The bond between two identical non-metal atoms has a pair of electrons : *(1986 - 1 Mark)*

(a) unequally shared between the two

(b) transferred fully from one atom to another

(c) with identical spins

(d) equally shared between them

17. The hydrogen bond is strongest in : *(1986 - 1 Mark)*

(a) O–H..........S (b) S–H..........O

(c) F–H..........F (d) F–H..........O

18. The hybridisation of sulphur in sulphur dioxide is : *(1986 - 1 Mark)*

(a) sp (b) sp^3 (c) sp^2 (d) dsp^2

19. Hydrogen bonding is maximum in *(1987 - 1 Mark)*

(a) Ethanol (b) Diethyl ether

(c) Ethyl chloride (d) Triethylamine

20. The species in which the central atom uses sp^2 hybrid orbitals in its bonding is *(1988 - 1 Mark)*

(a) PH_3 (b) NH_3 (c) CH_3^+ (d) SbH_3

21. The molecule that has linear structure is *(1988 - 1 Mark)*

(a) CO_2 (b) NO_2 (c) SO_2 (d) SiO_2

22. The molecule which has zero dipole moment is :

(a) CH_2Cl_2 (b) BF_3 *(1989 - 1 Mark)*

(c) NF_3 (d) ClO_2

23. The molecule which has pyramidal shape is :

(a) PCl_3 (b) SO_3 *(1989 - 1 Mark)*

(c) CO_3^{2-} (d) NO_3^-

24. The compound in which $\overset{*}{C}$ uses its sp^3 hybrid orbitals for bond formation is : *(1989 - 1 Mark)*

(a) $H\overset{*}{C}OOH$ (b) $(H_2N)_2\overset{*}{C}O$

(c) $(CH_3)_3\overset{*}{C}OH$ (d) $CH_3\overset{*}{C}HO$

25. Which of the following is paramagnetic? *(1989 - 1 Mark)*

(a) O_2^- (b) CN^- (c) CO (d) NO^+

26. The type of hybrid orbitals used by the chlorine atom in ClO_2^- is *(1992 - 1 Mark)*

(a) sp^3 (b) sp^2

(c) sp (d) none of these

27. The maximum possible number of hydrogen bonds a water molecule can form is *(1992 - 1 Mark)*

(a) 2 (b) 4 (c) 3 (d) 1

28. The cyanide ion, CN^- and N_2 are isoelectronic. But in contrast to CN^-, N_2 is chemically inert, because of *(1992 - 1 Mark)*

(a) low bond energy

(b) absence of bond polarity

(c) unsymmetrical electron distribution

(d) presence of more number of electrons in bonding orbitals

29. Pick out the isoelectronic structures from the following; *(1993 - 1 Mark)*

I. CH_3^+ II. H_3O^+

III. NH_3 IV CH_3^-

(a) I and II (b) III and IV

(c) I and III (d) II, III and IV

30. Which one is most ionic : *(1995S)*

(a) P_2O_5 (b) CrO_3 (c) MnO (d) Mn_2O_7

31. Number of paired electrons in O_2 molecule is : *(1995S)*

(a) 7 (b) 8 (c) 16 (d) 14

32. Among the following species, identify the isostructural pairs.

NF_3, NO_3^-, BF_3, H_3O^+, HN_3 *(1996 - 1 Mark)*

(a) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$

(b) $[NF_3, HN_3]$ and $[NO_3^-, BF_3]$

(c) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$

(d) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$

33. The number and type of bonds between two carbon atoms in CaC_2 are : *(1996 - 1 Mark)*

(a) one sigma (σ) and one pi (π) bonds

(b) one sigma (σ) and two pi (π) bonds

(c) one sigma (σ) and one and a half pi (π) bonds

(d) one sigma (σ) bond.

34. Which contains both polar and non-polar bonds?

(a) NH_4Cl (b) HCN *(1997 - 1 Mark)*

(c) H_2O_2 (d) CH_4

35. The critical temperature of water is higher than that of O_2 because the H_2O molecule has *(1997 - 1 Mark)*

(a) fewer electrons than O_2

(b) two covalent bonds

(c) V-shape (d) dipole moment.

36. Which one of the following compounds has sp^2 hydridization? *(1997 - 1 Mark)*

(a) CO_2 (b) SO_2 (c) N_2O (d) CO

37. The geometry and the type of hybrid orbital present about the central atom in BF_3 is *(1998 - 2 Marks)*

(a) linear, sp (b) trigonal planar, sp^2

(c) tetrahedral, sp^3 (d) pyramidal, sp^3.

38. The correct order of increasing C — O bond length of CO, CO_3^{2-}, CO_2, is *(1999 - 2 Marks)*

(a) $CO_3^{2-} < CO_2 < CO$ (b) $CO_2 < CO_3^{2-} < CO$

(c) $CO < CO_3^{2-} < CO_2$ (d) $CO < CO_2 < CO_3^{2-}$

39. The geometry of H_2S and its dipole moment are *(1999 - 2 Marks)*

(a) angular and non-zero (b) angular and zero

(c) linear and non-zero (d) linear and zero

40. Molecular shapes of SF_4, CF_4 and XeF_4 are *(2000S)*
(a) the same, with 2, 0 and 1 lone pairs of electrons respectively
(b) the same, with 1, 1 and 1 lone pairs of electrons respectively
(c) different, with 0, 1 and 2 lone pairs of electrons respectively
(d) different, with 1, 0 and 2 lone pairs of electrons respectively

41. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are *(2000S)*
(a) sp, sp^3 and sp^2 respectively
(b) sp, sp^2 and sp^3 respectively
(c) sp^2, sp and sp^3 respectively
(d) sp^2, sp^3 and sp respectively

42. The common features among the species CN^-, CO and NO^+ are *(2001S)*
(a) bond order three and isoelectronic
(b) bond order three and weak field ligands
(c) bond order two and π–acceptors
(d) isoelectronic and weak field ligands

43. The correct order of hybridization of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is *(2001S)*
(a) dsp^2, dsp^3, sp^2 and sp^3 (b) sp^3, dsp^2, dsp^3, sp^2
(c) dsp^2, sp^2, sp^3, dsp^3 (d) dsp^2, sp^3, sp^2, dsp^3

44. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3
(a) N : tetrahedral, sp^3; B : tetrahedral, sp^3 *(2002S)*
(b) N : pyramidal, sp^3; B : pyramidal, sp^3
(c) N : pyramidal, sp^3; B : planar, sp^2
(d) N : pyramidal, sp^3; B : tetrahedral, sp^3

45. Identify the least stable ion amongst the following : *(2002S)*
(a) Li^- (b) Be^- (c) B^- (d) C^-

46. Which of the following molecular species has unpaired electron(s) ? *(2002S)*
(a) N_2 (b) F_2 (c) O_2^- (d) O_2^{2-}

47. Which of the following are isoelectronic and isostructural? $NO_3^-, CO_3^{2-}, ClO_3^-, SO_3$ *(2003S)*
(a) NO_3^-, CO_3^{2-} (b) SO_3, NO_3^-
(c) ClO_3^-, CO_3^{2-} (d) CO_3^{2-}, SO_3

48. According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding O_2^+ *(2004S)*
(a) Paramagnetic and Bond order < O_2
(b) Paramagnetic and Bond order > O_2
(c) Diamagnetic and Bond order < O_2
(d) Diamagnetic and Bond order > O_2

49. Which species has the maximum number of lone pair of electrons on the central atom? *(2005S)*
(a) $[ClO_3]^-$ (b) XeF_4 (c) SF_4 (d) $[I_3]^-$

50. Among the following, the paramagnetic compound is *(2007)*
(a) Na_2O_2 (b) O_3 (c) N_2O (d) KO_2

51. The species having bond order different from that in CO is *(2007)*
(a) NO^- (b) NO^+ (c) CN^- (d) N_2

52. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is *(2010)*
(a) 1 and diamagnetic (b) 0 and dimagnetic
(c) 1 and paramagnetic (d) 0 and paramagnetic

53. The species having pyramidal shape is : *(2010)*
(a) SO_3 (b) BrF_3 (c) SiO_3^{2-} (d) OSF_2

54. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O, respectively, are *(2011)*
(a) octahedral, tetrahedral and square planar
(b) tetrahedral, square planar and octahedral
(c) square planar, tetrahedral and octahedral
(d) octahedral, square planar and octahedral

55. Assuming 2*s*-2*p* mixing is **NOT** operative, the paramagnetic species among the following is *(JEE Adv. 2014)*
(a) Be_2 (b) B_2 (c) C_2 (d) N_2

56. The geometries of the ammonia complexes of Ni^{2+}, Pt^{2+} and Zn^{2+} respectively, are *(JEE Adv. 2016)*
(a) octahedral, square planar and tetrahedral
(b) square planar, octahedral and tetrahedral
(c) tetrahedral, square planar and octahedral
(d) octahedral, tetrahedral and square planar

D MCQs with One or More Than One Correct

1. CO_2 is isostructural with : *(1986 - 1 Mark)*
(a) $HgCl_2$ (b) $SnCl_2$ (c) C_2H_2 (d) NO_2

2. The linear structure is assumed by : *(1991 - 1 Mark)*
(a) $SnCl_2$ (b) NCO^- (c) CS_2 (d) NO_2^+

3. Which of the following have identical bond order? *(1992 - 1 Mark)*
(a) CN^- (b) O_2^- (c) NO^+ (d) CN^+

4. The molecules that will have dipole moment are *(1992 - 1 Mark)*
(a) 2, 2-dimethylpropane (b) trans-2-pentene
(c) cis-3-hexene (d) 2,2,3,3-tetramethylbutane

5. The compound(s) with TWO lone pairs of electrons on the central atom is(are) *(JEE Adv. 2016)*
(a) BrF_5 (b) ClF_3 (c) XeF_4 (d) SF_4

6. According to Molecular Orbital Theory, *(JEE Adv. 2016)*
(a) C_2^{2-} is expected to be diamagnetic
(b) O_2^{2+} is expected to have a longer bond length than O_2
(c) N_2^+ and N_2^- have the same bond order
(d) He_2^+ has the same energy as two isolated He atoms

E Subjective Problems

1. Water is liquid while H_2S is a gas at room temperature. *(1978)*

2. Write the Lewis dot structural formula for each of the following. Give, also, the formula of a neutral molecule, which has the same geometry and the same arrangement of the bonding electrons as in each of the following. An example is given below in the case of H_3O^+ :

Lewis dot structure

Neutral molecule

(i) O_2^{2-} ; (ii) CO_3^{2-} ; (iii) CN^-; (iv) NCS^-

(1983 - 1 × 4 = 4 Marks)

3. How many sigma bonds and how many pi-bonds are present in a benzene molecule? *(1985 - 1 Mark)*
4. Write the Lewis dot structure of the following :

$O_3, COCl_2$

(1986 - 1 Mark)

5. Arrange the following :
   (i) N_2, O_2, F_2, Cl_2 in increasing order of bond dissociation energy. *(1988 - 1 Mark)*
   (ii) Increasing strength of hydrogen bonding (X–H–X) : *(1991 - 1 Mark)*

   O, S, F, Cl, N

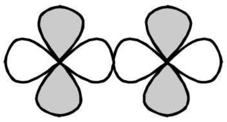
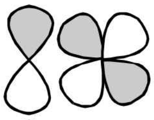
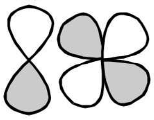
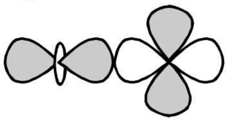
   (iii) In the decreasing order of the O – O bond length present in them *(2004 - 4 Marks)*

   O_2, KO_2 and $O_2\,[AsF_4]$

6. The dipole moment of KCl is 3.336×10^{-29} Coulomb meters which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl. *(1993 - 2 Marks)*
7. Using the VSEPR theory, identify the type of hybridization and draw the structure of OF_2. What are the oxidation states of O and F ? *(1994 - 3 Marks)*
8. A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. *(1997 - 2 Marks)*
9. Interpret the non-linear shape of H_2S molecule and non-planar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory. (Atomic numbers : H = 1, P = 15, S = 16, Cl = 17.) *(1998 - 4 Marks)*
10. Write the M.O. electron distribution of O_2. Specify its bond order and magnetic property. *(2000 - 3 Marks)*
11. Using VSEPR theory, draw the shape of PCl_5 and BrF_5. *(2003 - 2 Marks)*
12. Draw the structure of XeF_4 and OSF_4 according to VSEPR theory, clearly indicating the state of hybridisation of the central atom and lone pair of electrons (if any) on the central atom. *(2004 - 2 Marks)*

F Match the Following

1. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists. *(JEE Adv. 2014)*

	List-I	List-II
P.		1. $p - d\,\pi$ antibonding
Q.		2. $d - d\,\sigma$ bonding
R.		3. $p - d\,\pi$ bonding
S.		4. $d - d\,\sigma$ antibonding

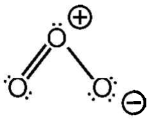
Code:

	P	Q	R	S
(a)	2	1	3	4
(b)	4	3	1	2
(c)	2	3	1	4
(d)	4	1	3	2

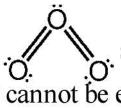
H Assertion & Reason Type Questions

1. Read the following Assertion and Reason and answer as per the options given below : *(1998 - 2 Marks)*

Assertion : The electronic structure of O_3 is



Reason :



structure is not allowed because octet around O cannot be expanded.

(a) If both *assertion* and *reason* are correct, and *reason* is the correct explanation of the *assertion*.
(b) If both *assertion* and *reason* are correct, but *reason* is not the correct explanation of the *assertion*.
(c) If *assertion* is correct but *reason* is incorrect.
(d) If *assertion* is incorrect but *reason* is correct.

2. Read the following Assertion and Reason and answer as per the options given below : *(1998 - 2 Marks)*

Assertion : LiCl is predominantly a covalent compound.
Reason : Electronegativity difference between Li and Cl is too small.

(a) If both *assertion* and *reason* are correct, and *reason* is the correct explanation of the *assertion*.
(b) If both *assertion* and *reason* are correct, but *reason* is not the correct explanation of the *assertion*.
(c) If *assertion* is correct but *reason* is incorrect.
(d) If *assertion* is incorrect but *reason* is correct.

I Integer Value Correct Type

1. Based on VSEPR theory, the number of 90 degree F–Br–F angles in BrF_5 is *(2010)*
2. The total number of lone-pairs of electrons in melamine is *(JEE Adv. 2013)*

3. A list of species having the formula XZ_4 is given below.
XeF_4, SF_4, SiF_4, BF_4^-, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$.
Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is *(JEE Adv. 2014)*

4. Among the triatomic molecules/ions, $BeCl_2$, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^- and XeF_2, the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital(s) is
[Atomic number : S = 16, Cl = 17, I = 53 and Xe = 54]
(JEE Adv. 2015)

Section-B JEE Main / AIEEE

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
(a) Charge on the ion and size of the ion **[2005]**
(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 $p\pi - p\pi$ 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 $p\pi - p\pi$ 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. Among the following the maximum covalent character is shown by the compound **[2011]**
(a) $FeCl_2$ (b) $SnCl_2$ (c) $AlCl_3$ (d) $MgCl_2$

25. The hybridization of orbitals of N atom in NO_3^-, NO_2^+ and NH_4^+ are respectively : **[2011]**
(a) sp, sp^2, sp^3 (b) sp^2, sp, sp^3
(c) sp, sp^3, sp^2 (d) sp^2, sp^3, sp

26. The structure of IF_7 is **[2011]**
(a) square pyramidal (b) trigonal bipyramidal
(c) octahedral (d) pentagonal bipyramidal

27. 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.

28. 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

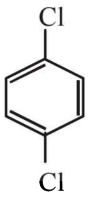
29. Which one of the following molecules is expected to exhibit diamagnetic behaviour ? **[JEE M 2013]**
(a) C_2 (b) N_2
(c) O_2 (d) S_2

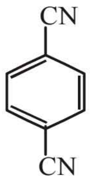
30. Which of the following is the wrong statement ? **[JEE M 2013]**
(a) ONCl and ONO^- are not isoelectronic.
(b) O_3 molecule is bent
(c) Ozone is violet-black in solid state
(d) Ozone is diamagnetic gas.

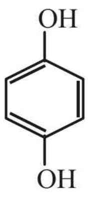
31. In which of the following pairs of molecules/ions, both the species are not likely to exist ? **[JEE M 2013]**
(a) H_2^+, He_2^{2-} (b) H_2^-, He_2^{2-}
(c) H_2^{2+}, He_2 (d) H_2^-, He_2^{2+}

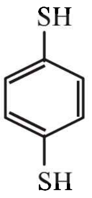
32. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of : **[JEE M 2013]**
(a) $Li_2 < Li_2^+ < Li_2^-$ (b) $Li_2^- < Li_2^+ < Li_2$
(c) $Li_2 < Li_2^- < Li_2^+$ (d) $Li_2^- < Li_2 < Li_2^+$

33. For which of the following molecule significant $\mu \neq 0$? **[JEE M 2014]**

(i) 

(ii) 

(iii) 

(iv) 

(a) Only (i) (b) (i) and (ii)
(c) Only (iii) (d) (iii) and (iv)

34. 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^-

4 Chemical Bonding and Molecular Structure

Section-A : JEE Advanced/ IIT-JEE

A **1.** CO_2 **2.** HCOOH and CH_3COOH **3.** 2 **4.** sp^3 **5.** planar
6. Three centred two electron bond or banana bond **7.** Increases, decreases
B **1.** T **2.** F **3.** T **4.** F **5.** F **6.** F **7.** F
C **1.** (c) **2.** (d) **3.** (a) **4.** (a) **5.** (c) **6.** (b) **7.** (c) **8.** (a)
9. (a) **10.** (b) **11.** (b) **12.** (d) **13.** (c) **14.** (b) **15.** (a) **16.** (d)
17. (c) **18.** (c) **19.** (a) **20.** (c) **21.** (a) **22.** (b) **23.** (a) **24.** (c)
25. (a) **26.** (a) **27.** (b) **28.** (b) **29.** (d) **30.** (c) **31.** (d) **32.** (c)
33. (b) **34.** (c) **35.** (d) **36.** (b) **37.** (b) **38.** (d) **39.** (a) **40.** (d)
41. (b) **42.** (a) **43.** (b) **44.** (a) **45.** (b) **46.** (c) **47.** (a) **48.** (b)
49. (d) **50.** (d) **51.** (a) **52.** (a) **53.** (d) **54.** (b) **55.** (c) **56.** (a)
D **1.** (a, c) **2.** (b, c, d) **3.** (a, c) **4.** (b, c) **5.** (b, c) **6.** (a, c)
E **3.** $12\sigma, 6\pi$ **5.** (i) $F_2 < Cl_2 < O_2 < N_2$; (ii) $S < Cl < N < O < F$; (iii) $O_2[AsF_4] > O_2 > KO_2$
6. 80.09% **7.** +2, –1 **8.** $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$ **10.** 2
F **1.** (c)
H **1.** (a) **2.** (c)
I **1.** 0 **2.** 6 **3.** 4 **4.** 4

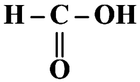
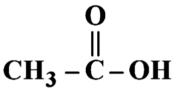
Section-B : JEE Main/ AIEEE

1. (a) **2.** (b) **3.** (a) **4.** (c) **5.** (b) **6.** (b) **7.** (a) **8.** (a)
9. (b) **10.** (b) **11.** (a) **12.** (d) **13.** (a) **14.** (c) **15.** (d) **16.** (b)
17. (b) **18.** (d) **19.** (c) **20.** (c) **21.** (a) **22.** (b) **23.** (d) **24.** (c)
25. (b) **26.** (d) **27.** (b) **28.** (c) **29.** (a) **30.** (a) **31.** (c) **32.** (b)
33. (d) **34.** (c)

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **CO_2;** Bond angle in CH_4 is 109°.28’, in H_2O it is 105 and in CO_2 it is 180°. So it is maximum in case of CO_2

2. **$H-\underset{\underset{O}{\|}}{C}-OH$** and **$CH_3-\overset{\overset{O}{\|}}{C}-OH$** form strongest hydrogen bonds because of largest difference in electronegativities of bonded atoms.

3. **2;** $N \equiv N$ (N_2) has 1σ and 2π bonds. (A triple bond consists of 1σ and 2π bonds)

4. **sp^3;** Hybridisation (H)= $\frac{1}{2}$ [No. of valence electron in central atom + No. of monovalent atoms – Charge on cation + Charge on anion]

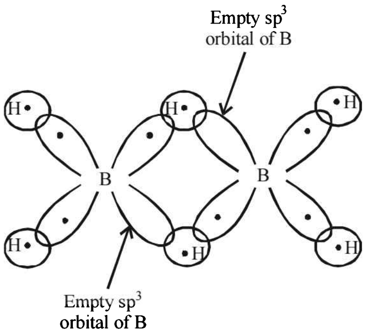
For N in NH_4^+, hybridisation (H) = $\frac{1}{2}(5+4-1+0)=4$

$\therefore$ sp^3 hybridisation.

5. **Planar;** $\overset{+}{C}H_3$ is a carbocation and such a species has a planar shape.

6. Three centred two electron bonds or **banana bond;**

NOTE : The formation of three centred two electron bond is due to one empty *sp*^{3} orbital of one of the B atom, 1*s* orbital of the bridge hydrogen atom and one of the *sp*^{3} (filled) orbital of the other B-atom. This forms a delocalized orbital covering the three nuclei giving the shape of a banana. Thus also known as banana bonds.



7. **Increases, decreases;**

$\therefore$ Bond order in $N_2 = 3$ and Bond order in $N_2^+ = 2.5$

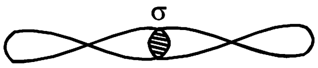
Thus conversion of N_2 to N_2^+ decreases bond order (from 3 to 2.5) and hence increases the N – N bond distance. [$\because$ Bond distance increases with decrease in B.O.)

Bond order in $O_2 = 2$ and Bond order in $O_2^+ = 2.5$

NOTE : Thus conversion of O_2 to O_2^+ increases bond order (from 2 to 2.5) hence decrease O – O bond distance.

B. True / False

1. **True :** Sigma bond is formed by the overlapping of two *s*-orbitals or one *s* and one *p* or the two *p* orbitals of the two different atoms. Thus linear overlap of two *p*-orbitals results in formation of a σ– bond.



Axial p-p overlapping

2. **False :** Symmetrical molecules with polar bonds have zero dipole moment.
3. **True :** $SnCl_2$ has 2 bond pairs and one lone pair of electrons. It is sp^2 hybridised and is trigonal planar in shape.
4. **False :** Only two orbitals are used since C in benzene is in sp^2 hybridised state.
5. **False :** sp^2 hybrid orbitals do not have equal *s* and *p* character. They have 33.3% *s*-character and 66.7% *p*-character.
6. **False :** The presence of polar bonds in a polyatomic molecule does not always lead to a definite dipole moment. This is because the dipole moment is a vector quantity and when the bond moment of one bond is cancelled by the equal but opposite bond moment due to other bond(s), the molecule has zero dipole moment, *e.g.* CO_2, CH_4, CCl_4 etc.
7. **False :** The C – F distance is less than the C – Cl, although the former involves more charge separation. However, here bond distance has more dominating effect causing dipole moment of CH_3Cl to be more than that of CH_3F.

C. MCQ with One Correct Answer

1. **(c)** In KCN, ionic bond is present between K^+ and CN^- and covalent bonds are present between carbon and nitrogen $C \equiv N$.
2. **(d)** $\because$ after forming the bonds, C has only 6 e^- in its valence shell.
3. **(a)** X^+Y^-
   $\because$ Electropositive elements forms cation and electronegative elements forms anion.
   Except this all compounds are ionic.
4. **(a)** H_2 H – H
5. **(c)** $N \equiv N$ $:N\vdots\vdots N:$
6. **(b)** $\because$ It forms hydrogen bonds with water
7. **(c)** **NOTE :** Dipole moment is vector quantity
   In trigonal planar geometry (for sp^2 hybridisation), the vector sum of two bond moments is equal and opposite to the dipole moment of third bond.
8. **(a)** **NOTE :** Isoelectronic species have same number of electrons.
   Electrons in CO = 6 + 8 = 14
   Electrons in CN^- = 6 + 7 + 1 = 14
   Electrons in O_2^- = 8 + 8 + 1 = 17
   Electrons in O_2^+ = 8 + 8 – 1 = 15
   $\therefore$ CO and CN^- are isoelectronic.
9. **(a)** **TIPS/Formulae :**

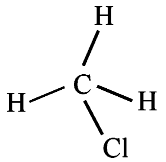
   $$\text{Hybridisation} = \frac{1}{2}(V + M - C + A)$$

   where; V = no. of electron in valence shell of central atom
   M = no. of monovalent atoms, C = charge on cation,
   A = charge on anion

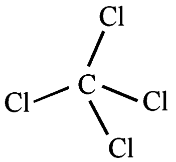
   (i) $CO_2, H = \frac{1}{2}(4 + 0 - 0 + 0) = 2$
   $\therefore$ sp hybridisation

   (ii) $SO_2, H = \frac{1}{2}(6 + 0 - 0 + 0) = 3$
   $\therefore$ sp^2 hybridisation

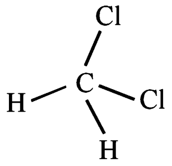
   (iii) NO_2 has V shaped structure.
   (iv) ClO_2 has V shaped structure.
   $\therefore$ CO_2 having sp hybridation has linear shape.
10. **(b)** **TIPS/Formulae :**
   (i) Dipole moment is vector quantity. When vector sum of all dipoles in molecule will be zero, then molecule will not have net dipole moment.
   (ii) **NOTE :** For net dipole moment to be equal to zero, all the atoms attached to central atom must be identical and geometry must be regular.



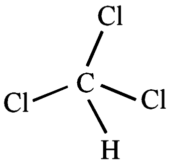
Methyl chloride



Carbon tetrachloride



Methylene chloride



Chloroform

∴ Carbon tetrachloride having regular geometry and identical atoms attached to bonds has zero dipole moment.

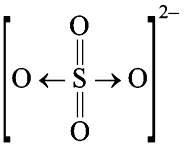
11. (b) In regular tetrahedral structure, dipole moment of one bond is cancelled by opposite dipole moment of the other bonds.

12. (d) **TIPS/Formulae :** Hydrogen bonding is formed in those compounds in which F or O or N atoms are attached to hydrogen atom.

∵ HCl does not have F or N or O

∴ It does not form hydrogen bond.

13. (c) Ionic bond or electrovalent between Cu^{2+} and SO_4^{2-},

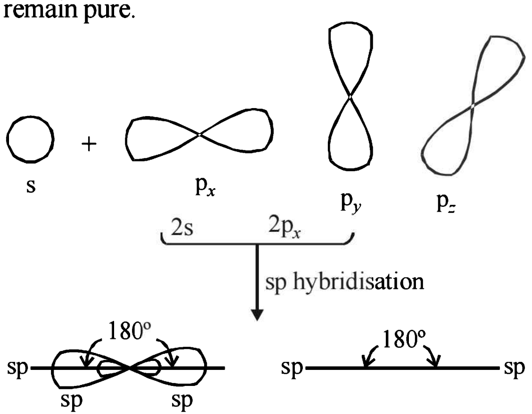
covalent and coordinate in SO_4^{2-}; 

$$\left[O \leftarrow \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} \rightarrow O \right]^{2-}$$

ion.

14. (b) **TIPS/Formulae :** *sp* type of hybridization involves the intermixing of one *s* and one *p* (say p_x) orbitals to give two equivalent hybrid orbitals, known as *sp* hybrid orbitals.

The two *sp* hybrid orbitals are directed diagonally, i.e., in a straight line with an angle of 180° **(collinear orbitals)**. The other two *p* orbitals (say p_y and p_z) remain pure.



15. (a) **NOTE THIS STEP :** Write the electronic configuration of each species according to molecular orbital theory.

NO ($15e^-$)– $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$

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

1 unpaired electron.

CO ($14e^-$)– $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$

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

no unpaired electron

CN^- ($14e^-$) – $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$

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

O_2 ($16e^-$) – $\sigma\ 1s^2,\ \sigma^*\ 1s^2,\ \sigma\ 2s^2,\ \sigma^*\ 2s^2,\ \sigma 2p_x^2,$ $\{\pi\, 2p_y^2 = \pi\, 2p_z^2, \{\pi^*\, 2p_y^1 = \pi^*\, 2p_z^1;$

Two unpaired electrons.

16. (d) In covalent bonds between two identical non-metal atoms share the pair of electrons equally between them, e.g. : F_2, O_2, N_2.

17. (c) **NOTE :** Greater the difference between electronegativities of two covalently bonded atoms more will be strength of hydrogen bond.

∴ F – H ....F bond is strongest due to largest difference in electronegativity of atoms and smallest size of F atom.

18. (c) **TIPS/Formulae :** $H = \frac{1}{2}(V + M - C + A)$

For SO_2, $H = \frac{1}{2}(6 + 0 + 0 - 0) = 3$

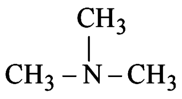
∴ sp^2 hybridisation.

19. (a) **NOTE :** Compounds having F or O or N attached to H form hydrogen bond.

CH_3CH_2OH ethanol

$C_2H_5-O-C_2H_5$ diethyl ether

CH_3CH_2Cl ethyl chloride



$$CH_3-\overset{\overset{CH_3}{|}}{N}-CH_3$$

Trimethyl amine

∴ Ethanol having H attached to O atom will form hydrogen bond. Rest of the compounds do not hydrogen bonds.

20. (c) From amongst given species PH_3, NH_3 and SbH_3 are all sp^3 hybridised. Their central atom has both bond pair as well as lone pair of electrons. The lone pair occupy the fourth orbital. CH_3^+ has only three pairs of electrons so it is sp^2 hybridised.

21. (a) **TIPS/Formulae :** Compound having sp hybridisation will have linear shape.

∴ CO_2 or (O=C=O) which has C in sp hybrid state has linear shape.

22. (b) **TIPS/Formulae :** Dipole moment of compound having regular geometry and same type of atoms is zero. It is vector quantity.

The zero dipole moment of BF_3 is due to its symmetrical (triangular planar) structure. The three fluorine atoms lie at the corners of an equilateral triangle with boron at the centre.

NOTE : The vectorial addition of the dipole moments of the three bonds gives a net sum of zero because the resultant of any two dipole moments is equal and opposite to the third. The dipole moment of NH_3 is 1.46 D indicating its unsymmetrical structure. The dipole moment of CH_2Cl_2 (the molecule uses sp^3 hybridisation but is not symmetric) is 1.57D.

23. (a) **TIPS/Formulae :**

Molecule having sp^3 hybridisation and one lone pair of electron will have pyramidal structure.

(i) CO_3^{2-} and NO_3^- have tetrahedron structure.

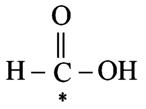
(ii) In PCl_3, P is sp^3 hybridised and has one lone pair of electrons, hence it is pyramidal in shape.

24. (c) **TIPS/Formulae :**

4σ bonds – sp^3 hybridisation

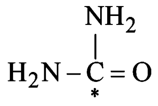
2σ and 2π bonds – sp^2 hybridisation

1σ and 3π bonds – sp hybridisation
[For hybridization only σ-bonds are considered]



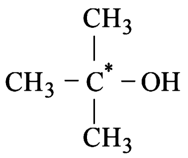
$H-\overset{\overset{O}{\|}}{\underset{*}{C}}-OH$

(a)



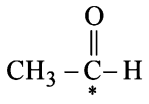
$H_2N-\overset{\overset{NH_2}{|}}{\underset{*}{C}}=O$

(b)



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^*}}-OH$

(c)



$CH_3-\overset{\overset{O}{\|}}{\underset{*}{C}}-H$

(d)

(a) 3σ, 1π (b) 3σ, 1π (c) 4σ (d) 3σ, 1π
∴ $(CH_3)_3COH$ has 4σ bonds and thus it has sp^3 hybridisation.

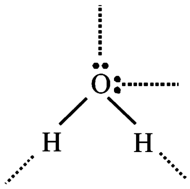
25. **(a)** O_2^- $(17e^-)-KK\sigma 2s^2\sigma^* 2s^2\sigma 2p_x{}^2$,
$\{\pi 2p_y{}^2=\pi 2p_z{}^2, \{\pi^* 2p_y{}^2=\pi^* 2p_z{}^1$
Thus, O_2^- has one unpaired electron; hence it is paramagnetic. Other species have no unpaired electron. All of them have 14 electrons.

26. **(a)** $H=\frac{1}{2}(V+M-C+A)$
where *H* = No. of orbitals involved in hybridisation (*viz.* 2, 3, 4, 5, 6) and hence nature of hybridisation (*viz.* sp^2, sp^3, sp^3d, sp^3d^2) can be ascertained.
V = No. of electrons in valence shell of the central atom, M = No. of monovalent atoms, C = Charge on cation, A = Charge on anion,

For ClO_2^-, we have, $H=\frac{1}{2}(7+0-0+1)$

$\Rightarrow H=\frac{1}{2}(7+1)=4$ or sp^3 hybridisation as 4 orbitals are involved

27. **(b)** H_2O molecule can form four hydrogen bonds per molecule, two via lone pairs and two via hydrogen atoms.



28. **(b)** In N_2, similar atoms are linked to each other and thus there is no polarity.

29. **(d)** No. of e^- in $CH_3{}^+=6+3-1=8$
No. of e^- in $H_3O^+=3+8-1=10$
No. of e^- in $NH_3=7+3=10$
No. of e^- in $CH_3{}^-=6+3+1=10$
∴ H_3O^+, NH_3 and $CH_3{}^-$ are isoelectronic.

30. **(c)** **TIPS/Formulae :**
(i) Non metallic oxides are more covalent (or less ionic) as compared to metallic oxides.
(ii) Higher the polarising power of cation (higher for higher oxidation state of similar size cations) more will be covalent character.

(i) P_2O_5 will be more covalent than other metallic oxides.
(ii) Oxidation state of Mn is + 7 in Mn_2O_7, oxidation state of Cr in CrO_3 is + 6 and oxidation state of Mn is + 2 in MnO.
∴ MnO is most ionic.

NOTE : P_2O_5, being a non-metallic oxide will definitely be more covalent than the other metallic oxides. Further, we know that higher the polarising power of the cation (higher for higher oxidation state of the similar size cations) more will be the covalent character. Here Mn is in +7 O.S in Mn_2O_7, Cr in +6 in CrO_3 and Mn in +2 in MnO. So MnO is the most ionic and Mn_2O_7 is the most covalent.

31. **(d)** O_2 = Oxygen (Z = 8) has following molecular orbital configuration of O_2.
$O_2\,(16e^-)=\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x{}^2, \{\pi 2p_y{}^2=\pi 2p_z{}^2, \{\pi^* 2p_y{}^1=\pi^* 2p_z{}^1$ i.e., 2 unpaired and 14 paired electrons.

32. **(c)** Structure of a molecule can be ascertained by knowing the number of hybrid bonds in the molecule. Thus

In NF_3 : $H=\frac{1}{2}(5+3-0+0)=4$

Thus N in NF_3 is sp^3 hybridized as 4 orbitals are involved in bonding.

In NO_3^- : $H=\frac{1}{2}(5+0-0+1)=3$

Thus N in NO_3^- is sp^2 hybridized as 3 orbitals are involved in bonding

In BF_3 : $H=\frac{1}{2}(3+3-0+0)=3$

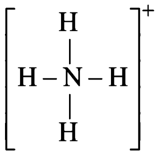
Thus B in BF_3 is sp^2 hybridized and 3 orbitals are involved in bonding

In H_3O^+ : $H=\frac{1}{2}(6+3-1+0)=4$

Thus O in H_3O^+ is sp^3 hybridized as 4 orbitals are involved in bonding.
Thus, isostructural pairs are [NF_3, H_3O^+] and [NO_3^-, BF_3].

33. **(b)** Calcium carbide is an ionic compound ($Ca^{2+}C^{2-}$) which produces acetylene on reacting with water. Thus the structure of C^{2-} is $[C\equiv C]^{2-}$. It has one σ and two π bonds. [∵ A triple bond consists of one σ and two π-bonds]

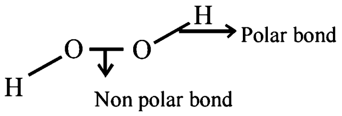
34. **(c)** (a)



$\left[H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-H\right]^+$ $[Cl]^-$ – It has ionic and non-polar covalent bond

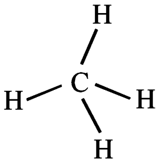
(b) $H-C\equiv N$ - It has ionic and polar covalent bonds.

(c)



It has polar and non polar both type of covalent bonds.

(d)



It has non polar covalent bonds only.

35. **(d)** Critical temperature of water is higher than O_2 because H_2O molecule has dipole moment which is due to its V-shape.

36. **(b)** **TIPS/Formulae :** $H = \frac{1}{2}(V + M - C + A)$

(i) $CO_2; H = \frac{1}{2}(4 + 0 - 0 + 0) = 2$

$\therefore$ sp hybridisation.

(ii) $SO_2; H = \frac{1}{2}(6 + 0 - 0 + 0) = 3$

$\therefore$ sp^2 hybridisation.

(iii) $CO; H = \frac{1}{2}(4 + 0 - 0 + 0) = 2$

$\therefore$ sp hybridisation.

37. **(b)** $H = \frac{1}{2}(3 + 3 + 0 - 0) = 3$

$\therefore$ Boron, in BF_3, is sp^2 hybridised leading to trigonal planar shape.

38. **(d)** **KEY CONCEPT**

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

(ii) Bond order is calculated by either the help of molecular orbital theory or by resonance.

(i) Bond order of CO as calculated by molecular orbital theory $= 3 \left\{ \text{b.o.} = \frac{1}{2}[N_b - N_a] \right\}$

(ii) Bond order of CO_2 (by resonance method)

$$= \frac{\text{No. of bonds in all possible sides}}{\text{No. of resonating structure}} = \frac{4}{2} = 2$$

(iii) Bond order in CO_3^{2-} (by resonance method)

$$= \frac{4}{3} = 1.33$$

$\therefore$ Order of bond length of C – O is $CO < CO_2 < CO_3^{2-}$

39. **(a)** Hybridisation of S in $H_2S = \frac{1}{2}(6 + 2 + 0 - 0) = 4$

$\therefore$ S has sp^3 hybridisation and 2 lone pair of electrons in H_2S

$\therefore$ It has angular geometry and so it has non-zero value of dipole moment.

40. **(d)** The structure of species can be predicted on the basis of hybridisation which in turn can be known by knowing the number of hybrid orbitals (H) in that species

$$H = \frac{1}{2}\left[\begin{array}{c} \text{No. of electrons} \\ \text{in valence} \\ \text{shell (H)} \end{array} + \begin{array}{c} \text{No. of mono-} \\ \text{valent atoms} \\ \text{(X)} \end{array} + \begin{array}{c} \text{charge} \\ \text{on} \\ \text{anion (A)} \end{array} - \begin{array}{c} \text{charge} \\ \text{on} \\ \text{cation (C)} \end{array}\right]$$

$$= \frac{1}{2}(6 + 4 + 0 - 0) = 5$$

For SF_4 : S is sp^3d hybridised in SF_4. Thus SF_4 has 5 hybrid orbitals of which only four are used by F, leaving one lone pair of electrons on sulphur.

For CF_4 : $H = \frac{1}{2}[4 + 4 + 0 - 0] = 4$ $\therefore$ sp^3 hybridisaion

Since all the four orbitals of carbon are involved in bond formation, no lone pair is present on C having four valence electrons

For XeF_4 : $H = \frac{1}{2}(8 + 4 + 0 - 0) = 6$, $\therefore$ sp^3d^2 hybridization of the six hybrid orbitals, four form bond with F, leaving behind two lone pairs of electrons on Xe.

41. **(b)** For NO_2^+ : $H = \frac{1}{2}(5 + 0 + 0 - 1) = 2$;

$\therefore$ sp hybridisation

For NO_3^- : $H = \frac{1}{2}[5 + 0 + 1 - 0) = 3$;

$\therefore$ sp^2 hybridisation

For NH_4^+ : $H = \frac{1}{2}[5 + 4 + 0 - 1] = 4$;

$\therefore$ sp^3 hybridisation

42. **(a)** Number of electrons in each species are

$CN^- = 6 + 7 + 1 = 14$, $CO = 6 + 8 = 14$

$NO^+ = 7 + 8 - 1 = 14$

Each of the species has 14 electrons which are distributed in MOs as below

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

Bond order $= \frac{10 - 4}{2} = 3$

43. **(b)** **TIPS/Formulae :** $H = \frac{1}{2}[V + M - C + A]$

Hybridisation of N in NH_3

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

Hybridisation of Pt in $[PtCl_4]^{2-}$

$= \frac{1}{2}[2 + 4 - 0 + 2] = 4$ $\therefore$ dsp^2

Hybridisation of P in PCl_5

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

Hybridisation of B in BCl_3

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

44. **(a)** $H_3N \rightarrow BF_3$ where both N, B are attaining tetrahedral geometry.

45. **(b)** **NOTE THIS STEP :** Write configuration of all species. Half filled and full filled orbitals are more stable as compared to nearly half filled and nearly full filled orbitals.

$Li^- = 1s^2, 2s^2$; $Be^- = 1s^2, 2s^2, 2p^1$
$B^- = 1s^2, 2s^2, 2p^2$; $C^- = 1s^2, 2s^2, 2p^3$
$\therefore$ Be^- will be least stable. It has lowest I.E.

46. **(c)** $N_2(7+7=14); \sigma 1s^2, \sigma 1^* s^2, \sigma 2s^2, \sigma^* 2s^2, \begin{cases} \pi^* 2p_y^2 \\ \pi^* 2p_z^2 \end{cases}, \sigma 2p_x^2$

$F_2(9+9=18); \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases},$

$$\begin{cases} \pi^* 2p_y^2 \\ \pi^* 2p_z^2 \end{cases}$$

$O_2^- (8+8+1=17); \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$

$$\begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^2 \\ \pi^* 2p_z^1 \end{cases}$$

$O_2^{2-} (8+8+2=18); \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$

$$\begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^2 \\ \pi^* 2p_z^2 \end{cases}$$

$\therefore$ O_2^- is the only species having unpaired electron.

47. **(a)** **NOTE :** Isoelectronic species have same number of electrons and isostructural species have same type of hybridisation at central atom.
NO_3^-; No. of $e^- = 7 + 8 \times 3 + 1 = 32$, hybridisation of N in NO_3^- is sp^3
CO_3^{2-}; No. of $e^- = 6 + 8 \times 3 + 2 = 32$, hybridisation of C in CO_3^{2-} is sp^3
ClO_3^-; No. of $e^- = 17 + 8 \times 3 + 1 = 42$, hybridisation of Cl in ClO_3^- is sp^3
SO_3; No. of $e^- = 16 + 8 \times 3 = 40$, hybridisation of S in SO_3 is sp^2
$\therefore$ NO_3^- and CO_3^{2-} are isostructural and isoelectronic.

48. **(b)** $O_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$

$$\begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^1 \end{cases}$$

Bond order $= \dfrac{10-6}{2} = 2$

(two unpaired electrons in antibonding molecular orbital)

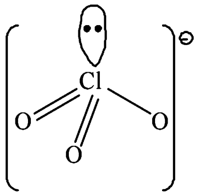
$O_2^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2, \\ \pi 2p_z^2, \end{cases} \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^0 \end{cases}$

Bond order $= \dfrac{10-5}{2} = 2.5$

(One unpaired electron in antibonding molecular orbital)

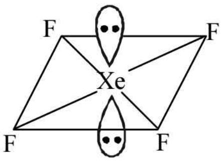
Hence O_2 as well as O_2^+ is paramagnetic, and bond order of O_2^+ is greater than that of O_2.

49. **(d)** ClO_3^-
(1 lone pair)



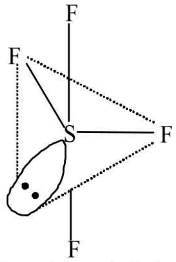
Pyramidal

XeF_4^-
(2 lone pair)



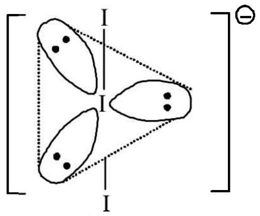
Square planar

SF_4
(1 lone pair)



Irregular tetrahedral

I_3^-
(3 lone pair)



Linear

50. **(d)** (i) In Na_2O_2, we have O_2^{2-} ion. Number of valence elctrons of the two oxygen in O_2^{2-} ion $= 8 \times 2 + 2$ $=18$ which are present as follows

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

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

$\therefore$ Number of unpaired electrons $= 0$, hence, O_2^{2-} is diamagnetic.

(ii) No. of valence electrons of all atoms in $O_3 = 6 \times 3 = 18$.
Thus, it also, does not have any unpaired electron, hence it is diamagnetic.

(iii) No. of valence electrons of all atom in N_2O $= 2 \times 5 + 6 = 16$. Hence, here also all electrons are paired. So it is diamagnetic.

(iv) In KO_2, we have O_2^- No. of valence electrons of all atoms in $O_2^- = 2 \times 6 + 1 = 13$,
Thus it has one unpaired electron, hence it is paramagnetic.

51. **(a)** Molecular electronic configuration of

$CO : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \{\pi 2p_y^2 = \pi 2p_z^2, \sigma 2p_x^2$

Therefore, bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-4}{2} = 3$

$NO^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \{\pi 2p_y^2 = \pi 2p_z^2$

Bond order $= \dfrac{10-4}{2} = 3$

$CN^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$

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

Bond order $= \frac{10-4}{2} = 3$

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

Bond order $= \frac{10-4}{2} = 3$

$NO^- : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$

$\{\pi 2p_y^2 = \pi 2p_z^2, \{\pi^* 2p_y^1 = \pi^* 2p_z^1$

Bond order $= \frac{10-6}{2} = 2$

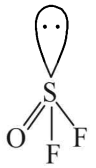
$\therefore$ NO^- has different bond order from that in CO.

52. (a) Molecular orbital configuration of $B_2(10)$ as per the condition will be

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

Bond order of $B_2 = \frac{6-4}{2} = 1$, B_2 will be diamagnetic.

53. (d) $OSF_2 : \frac{N}{2} = \frac{6+2}{2} = 4$. It has 1 lone pair.



(Shape is trigonal pyramidal)

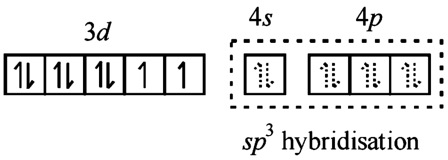
The shapes of SO_3, BrF_3 and SiO_3^{2-} are triangular planar respectively.

54. (b) $Ni^{+2} + 4Cl^- \longrightarrow \underset{sp^3}{[NiCl_4]^{2-}}$

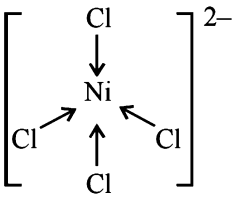
$[NiCl_4]^{2-}$. = $3d^8$ configuration with nickel in + 2 oxidation state, Cl^- being weak field ligand does not compel for pairing of electrons.

So,

$[NiCl_4]^{2-}$



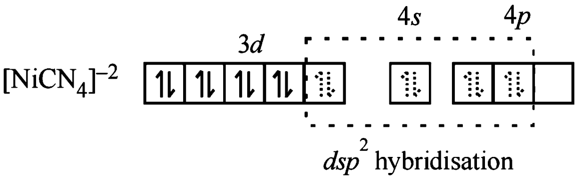
Hence, complex has tetrahedral geometry



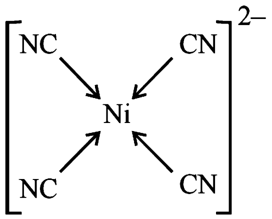
$Ni^{+2} + 4CN^- \longrightarrow [Ni(CN)_4]^{2-}$

$[Ni(CN)_4]^{2-}$ = $3d^8$ configuration with nickel in + 2 oxidation state, CN^- being strong field ligand compels for pairing of electrons.

So,

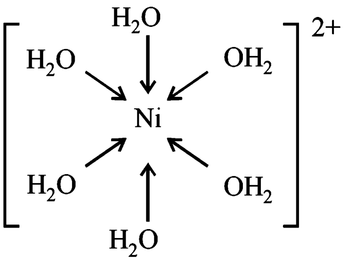


Hence, complex has square planar geometry.



$Ni^{+2} + 6H_2O \longrightarrow [Ni(H_2O)_6]^{2+}$

$[Ni(H_2O)_6]$ = $3d^8$ configuration with nickel in + 2 oxidation state. As with $3d^8$ configuration two d-orbitals are not available for d^2sp^3 hybridisation. So, hybridisation of Ni (II) is sp^3d^2 and Ni (II) with six co-ordination will have octahedral geometry.



Note : With water as ligand, Ni (II) forms octahedral complexes.

55. (c) $Be_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2$
$B_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma^2 p_z{}^2$
$C_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma^2 p_z{}^2\, \pi 2p_x{}^1\, \pi 2p_y{}^1$
$N_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma 2p_z{}^2\, \pi 2p_x{}^2\, \pi 2p_y{}^2$
Thus only C_2 will be paramagnetic

56. (a) Ni^{2+} with NH_3 shows CN = 6 forming $[Ni(NH_3)_6]^{2+}$ (Octahedral)

Pt^{2+} with NH_3 shows CN = 4 forming $[Pt(NH_3)_4]^{2+}$ (5d series CMA, square planner)

Zn^{2+} with NH_3 shows CN = 4 forming $[Zn(NH_3)_4]^{2+}$ ($3d^{10}$ configuration, tetrahedral)

D. MCQs with One or More than One Correct

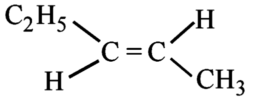
1. (a, c) CO_2, $HgCl_2$ and C_2H_2 have linear structure (sp hybridization), while $SnCl_2$ is trigonal planar (sp^2 hybridisation). NO_2 has angular structure (V-shape).

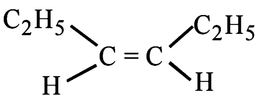
2. **(b,c,d)** $[O=N=O]^+$; $[N\equiv C-O]^-$; $S=C=S$
It can be seen from the structure shown above that CS_2 being *sp* hybridized has a linear shape and other two molecules are isoelectronic to CS_2, so they are also linear. $SnCl_2$ and SO_2 are sp^2 hybridised and are not linear.

3. **(a, c)** The outer most shells of C, N & O has 4, 5 and 6 electrons respectively. Thus CN^- and NO^+ each has 10 electrons to accommodate in the molecular orbitals.

So their bond order is same. O_2^- has 13 and CN^+ has 12 electrons in outermost orbits.

4. **(b, c)** Alkanes (a) and (d) don't have dipole moment because of symmetry in them.


trans 2-pentene


cis 3-hexene

These alkenes are not symmetrical and so they have dipole moment.

5. **(b, c)**

Compound		Number of lone pairs on central atom
BrF_5	→	1
ClF_3	→	2
XeF_4	→	2
SF_4	→	1

6. **(a, c)**
(A) The molecular orbital energy configuration of C_2^{2-} is

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

In the MO of C_2^{2-} there is no unpaired electron hence it is diamagnetic

(B) Bond order of O_2^{2+} is 3 and O_2 is 2 therefore bond length of O_2 is greater than O_2^{2+}

(C) The molecular orbital energy configuration of N_2^+ is

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

Bond order of $N_2^+ = \frac{1}{2}(9-4) = 2.5$

The molecular orbital energy configuration of N_2^- is

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

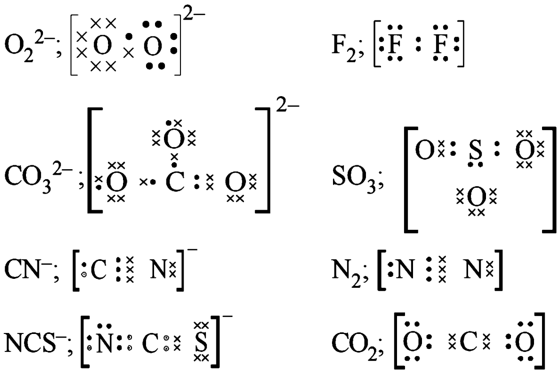
Bond order of $N_2^- = \frac{1}{2}(10-5) = 2.5$

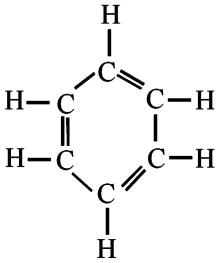
(D) He_2^+ has less energy in comparison to two isolated He atoms because some energy is released during the formation of He_2^+ from 2 He atoms.

E. Subjective Problems

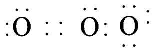
1. H_2O molecules are held together by hydrogen bonding which is stronger force of attraction but H_2S molecules are held together by vander waals forces of attraction, which are weaker forces. As a result water molecules come closer and exist in liquid state.

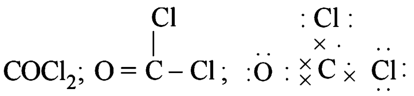
2. **Lewis dot structure** **Neutral molecule**



3. 
∴ It has 12σ and 3π bonds.

(6σ C–C bonds and 6σ C–H bonds)

4. O_3; $O=O \rightarrow O$; 



$COCl_2$; $O=\overset{\overset{Cl}{|}}{C}-Cl$;

5. (i) Increasing order of bond dissociation energy.
$F_2 < Cl_2 < O_2 < N_2$

NOTE : Fluorine-fluorine bond energy is less than the Cl–Cl because of larger repulsion between the non-bonded electrons of the two smaller fluorine atoms (chlorine atoms are larger in size; hence their lone pair of electrons exert less repulsion than fluorine). Oxygen having two pairs of lone pair of electrons on each atom exert less repulsion than that of chlorine or fluorine each having three lone pairs of electrons. Nitrogen having only one lone pair of electrons exert minimum repulsion, hence it is the most stable.

(ii) H-bonding is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (F, O, N). Further, higher the electronegativity and smaller the size of the atom, the stronger is the hydrogen bond.

NOTE : Although Cl has the same electronegativity as nitrogen, it does not form effective hydrogen bonds. This is because of its larger size than that of N with the result its electrostatic attractions are weak. Similarly, sulphur forms a very weak hydrogen bond due to its low electronegativity, although oxygen present in the same group forms a strong hydrogen bond.

Hence the order is $S < Cl < N < O < F$

(iii) In KO_2, O_2 is present as O_2^-, while in $\overset{+1}{O_2}(\overset{+3}{As}\,\overset{-4}{F_4})$, O_2 is present as O_2^+. Write down the MO configuration of O_2, O_2^- and O_2^+.

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

Thus the bond order $= \dfrac{10-6}{2} = 2$

O_2^- : Same as above except $\pi^* 2p_y^2, \pi^* 2p_z^1$ in place of $\pi^* 2p_y^1, \pi^* 2p_z^1$.

Thus the bond order in $O_2^- = \dfrac{10-7}{2} = 1.5$

O_2^+ : Same as in O_2 except $\pi^* 2p_y{}^1 = \pi^* 2p_z{}^0$ in place of $\pi^* 2p_y^1, \pi^* 2p_z^1$.

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

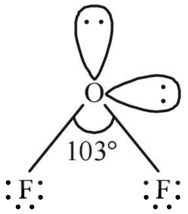
$\therefore$ Bond order in the three species is $O_2^+ > O_2 > O_2^-$
or $O_2[AsF_4] > O_2 > KO_2$

6. Dipole moment, $\mu = e \times d$ coulombs metre
For KCl $d = 2.6 \times 10^{-10}$ m
For complete separation of unit charge (electronic charge)
$(e) = 1.602 \times 10^{-19}$ C
Hence $\mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29}$ Cm
$\mu_{KCl} = 3.336 \times 10^{-29}$ Coulomb meter (given)

$$\therefore \text{ \% Ionic character of KCl} = \frac{3.336 \times 10^{-29}}{4.1652 \times 10^{-29}} \times 100$$

$$= \mathbf{80.09\%}$$

7. The structure of OF_2 is similar to H_2O and involves sp^3 hybridization on O atom. The bond angle in F – O – F is not exactly 109°28′, but distorted (103°) due to presence of lone pair of electrons on O as well as F leading to V shape or tetrahedral positions with two positions occupied by lone pair of electrons of the molecule.



Oxidation number of F = –1
$\therefore$ Oxidation number of O = +2

8. Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM
where $n \rightarrow$ number of unpaired electrons
μ = 1.73 BM for vanadium ion

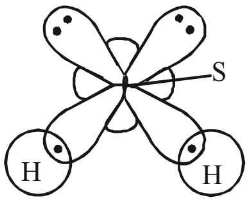
$1.73 \text{ BM} = \sqrt{n(n+2)}$ So, $(1.73)^2 = n(n+2)$
$3.0 = n^2 + 2n$ or $n^2 + 2n - 3 = 0$
$n^2 + 3n - n - 3 = 0$ $\therefore$ $n(n+3) - 1(n+3) = 0$
$(n-1)(n+3) = 0$ Correct value of $n = 1$
Thus no. of unpaired electrons in vanadium ion = 1
$_{23}V = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3, 4s^2$

It will have one unpaired electron if it will lose two electrons from 4*s* and two from 3*d*.
$\therefore$ Vanadium (IV) has one unpaired electron.
$V^{4+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$

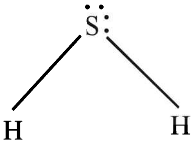
9. In H_2S, no. of hybrid orbitals $= \dfrac{1}{2}(6+2-0+0) = 4$

Hence here sulphur is sp^3 hybridised, so

$$_{16}S = 1s^2, 2s^2 2p^6, \underbrace{3s^2 3p_x^2 3p_y^1 3p_z^1}_{sp^3 \text{ hybridisation}}$$



or

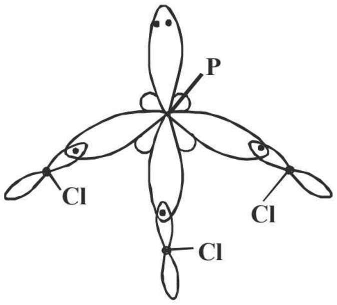


NOTE : Due to repulsion betwen *l*p - *l*p; the geometry of H_2S is distorted from tetrahedral to V-shape.

In PCl_3, no. of hybrid orbitals $= \dfrac{1}{2}[5+3-0+0] = 4$

Hence, here P shows sp^3 - hybridisation

$$_{15}P = 1s^2, 2s^2 2p^6, \underbrace{3s^2 3p_x^1 3p_y^1 3p_z^1}_{sp^3 \text{ hybridisation}}$$



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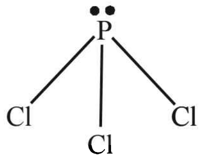


Thus due to repulsion between *l*p - bp, geometry is distorted from tetrahedral to pyramidal.

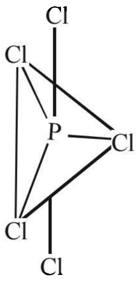
10. MO configuration of O_2 :

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

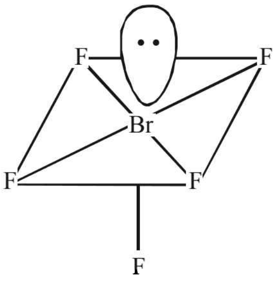
Bond order $= \dfrac{1}{2}(10-6) = 2$

Since O_2 molecule has two unpaired electrons, it is paramagnetic.

11.



PCl_5 : sp^3d Trigonal bipyramidal

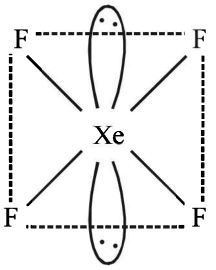


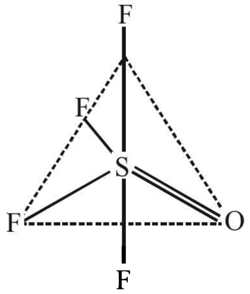
BrF_5 : sp^3d^2
Square pyramidal

12. First determine the total number of electron pairs around the central atom.

$$XeF_4 = \frac{N}{2} = \frac{8+4}{2} = 6$$

Thus in XeF_4, Xe is sp^3d^2 hybridised. The structure of the molecule is octahedral and shape is square planer with two lone pair of electrons.



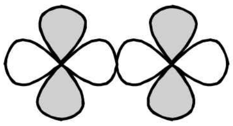


For $OSF_4 : \frac{N}{2} = \frac{6+4}{2} = 5$

Thus the central atom (S) is sp^3d hybridised leading to trigonal bipyramidal structure with no lone pair of electrons.

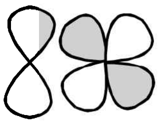
F. Match the Following

1. **(c)** **P.**



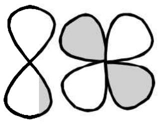
d – d (σ bonding)

Q.



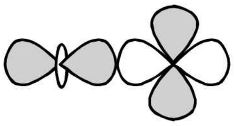
p – d (π bonding)

R.



p – d (π antibonding)

S.



d – d (σ antibonding)

H. Assertion & Reason Type Questions

1. **(a)** Both assertion and reason are correct. The reason explains the assertion as the central O-atom cannot have more than 8 electrons (octet).

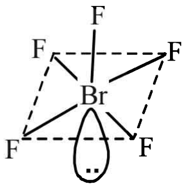
2. **(c)** LiCl is a covalent compound since due to the large size of the anion (Cl^-) its effective nuclear charge lessens and its valence shells are held less tightly towards its nucleus. Here, assertion is correct but reason is incorrect.

I. Integer Value Correct Type

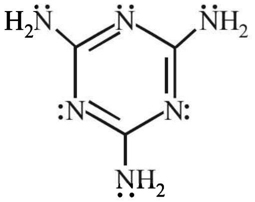
1. **(0)** According to VSEPR theory, number of electron pairs around central atom (Br) are 6.

$\frac{N}{2} = \frac{7+5}{2} = 6.$ (Five are bond pairs and one is lone pair)

Its geometry is octahedral but due to lone pair –bond pair repulsion, the four fluorine atoms at corner are forced towards the upper fluorine atom thus reducing F–Br–F angle from 90° to 84.8°.

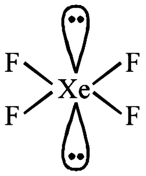
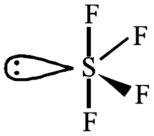
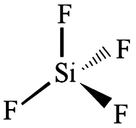
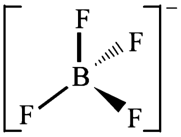
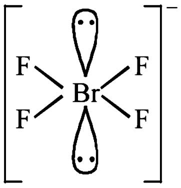
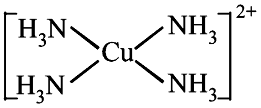
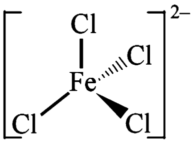


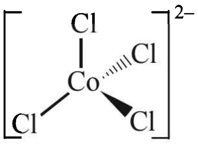
2. **(6)** Structure of melamine is as follows :

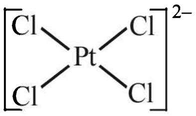


Total no. of lone pairs of electron is '6'.

3. **(4)**

XeF_4 :		Square planar (sp^3d^2)
SF_4 :		See-saw (sp^3d)
SiF_4 :		Tetrahedral (sp^3)
BF_4^- :		Tetrahedral (sp^3)
BrF_4^- :		Square planar (sp^3d^2)
$[Cu(NH_3)_4]^{2+}$:		Square planar (dsp^2)
$[FeCl_4]^{2-}$:		Tetrahedral (sp^3)

$[CoCl_4]^{2-}$:  Tetrahedral (*sp*^{3})

$[PtCl_4]^{2-}$:  Square planar (*dsp*^{2})

4. **(4)** $Cl-Be-Cl$

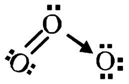
Hybridization *sp*
Structure linear

$N\equiv N-\ddot{\underset{\cdot\cdot}{N}}:^-$

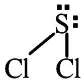
Hybridisation *sp*
Structure linear

$O=\overset{+}{N}\rightarrow O$

Hybridisation *sp*
Structure Linear



Hybridisation *sp*^{2}
Structure Trigonal planar



Hybridisation *sp*^{3}
Structure Angular

$[Cl-\ddot{I}-Cl]^-$

Hybridisation *sp*^{3}*d*
Structure linear

$[I-\ddot{I}-I]^-$

Hybridisation *sp*^{3}*d*
Structure Linear

$F-\ddot{Xe}-F$

Hybridisation *sp*^{3}*d*
Structure Linear

$\overset{-}{N}=\overset{+}{N}=O$

Hybridisation *sp*
Structure Linear

Only $BeCl_2$, N_3^-, N_2O and NO_2 are linear with *sp*-hybridisation.

Section-B JEE Main/ AIEEE

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 :**

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

(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,

$$\text{Hybridisation of O atom} = \frac{1}{2}[6+2-0+0]=4=sp^3$$

For H_3O^+, Hybridisation of O atom $= \frac{1}{2}[6+3-1+0]$
$=4=sp^3$

(c) For NH_3

$$\text{Hybridisation of N atom} = \frac{1}{2}[5+3-0+0]=4=sp^3$$

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.

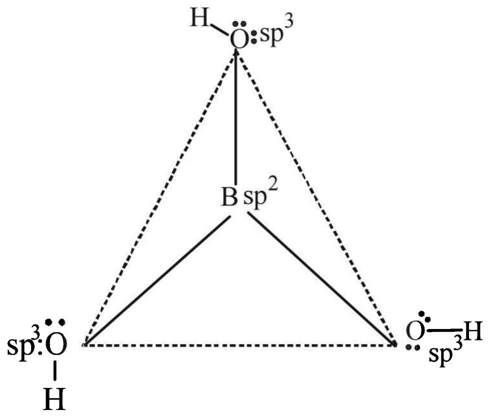
F—Xe—F O=C=O

8. **(a)** The order of bond angles

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

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)**

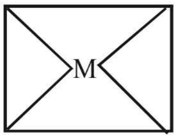


11. **(a)** XeF_4 (sp^3d^2 square planar),

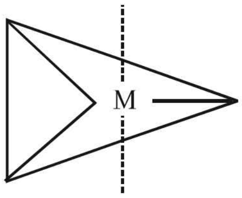
$[Ni(CN)_4]^{2-}$ (dsp^2 square planar),

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

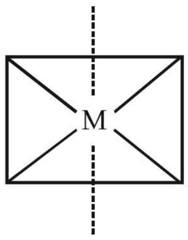
12. **(d)**



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) $\sigma^2\sigma^{*2}\sigma^2\sigma^{*2}\begin{matrix}\pi^2\\ \pi^2\end{matrix}\sigma^1\begin{matrix}\pi^*\\ \pi^*\end{matrix}\sigma^*$

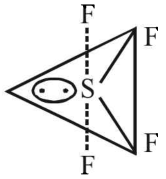
O_2 (electrons 16) $\sigma^2\sigma^{*2}\sigma^2\sigma^{*2}\sigma^2\begin{matrix}\pi^2\\ \pi^2\end{matrix}\begin{matrix}\pi^{*1}\\ \pi^{*1}\end{matrix}\sigma^*$

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

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

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

$$O_2 \to \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \{\pi 2p_y^2 = \pi 2p_z^2,$$
$$\{\pi^* 2p_y^1 = \pi^* 2p_z^1 - 2 \text{ unpaired electrons}$$

$$O_2^+ \to \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$$
$$\{\pi 2p_y^2 = \pi 2p_z^2 \{\pi^* 2p_y^1 = \pi^* 2p_z^0 - 1 \text{ unpaired electron}$$

$$NO \to \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2,$$
$$\{\pi 2p_y^2 = \pi 2p_z^2, \{\pi^* 2p_y^1 = \pi^* 2p_z^0 - 1 \text{ unpaired electron}$$

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 $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

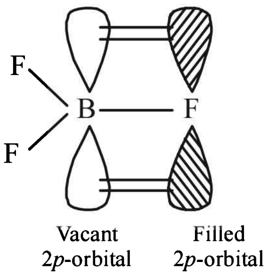
19. **(c)** (a) N_2 : bond order 3, paramagnetic
N_2^- : bond order, 2.5, paramagnetic
(b) C_2 : bond order 2, diamagnetic
C_2^+ : bond order 1.5, paramagnetic
(c) NO : bond order 2.5, paramagnetic
NO^+ : bond order 3, diamagnetic
(d) O_2 : bond order 2, paramagnetic
O_2^+ : bond order 2.5, paramagnetic

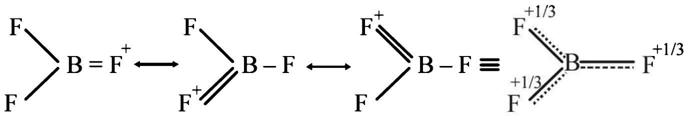
20. **(c)** **NOTE :** Greater the difference between electronegativity of bonded atoms, stronger will be bond. Since F is most electronegative hence F – H ...... F is the strongest bond.

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

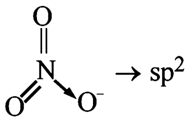
$\therefore$ Bond length is shortest in O_2^{2+}.

24. **(c)** The proportion of covalent character in an ionic bond is decided by polarisability of the metal cation as well as the electrongativity of both elements involved in bonding. Polarisability is further decided by the density of positive charge on the metal cation. $AlCl_3$ is considered to show maximum covalent character among the given compounds. This is because Al^{3+} bears 3 unit of positive charge and shows strong tendency to distort the electron cloud, thus the covalent character in Al-Cl bond dramatically increases.

25. **(b)** The formula to find the hybridisation of central atom is

$Z = \frac{1}{2}$ [Number of valence electrons on central atom + No. of monovalent atom altached to it + negative charge if any – positive charge if any]

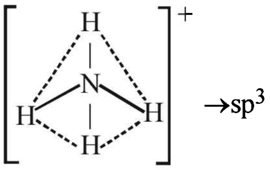
For NO_3^- $Z = \frac{1}{2}[5+0+1-0] = 3$



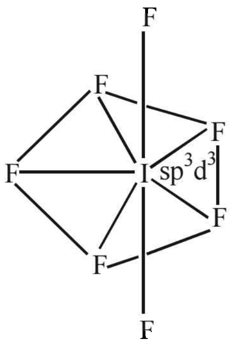
For NO_2^+, $Z = \frac{1}{2}[5+0+0-1] = 2$

$O = \overset{+}{N} = O \rightarrow sp$

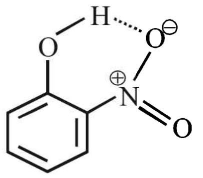
For NH_4^+, $Z = \frac{1}{2}[5+4+0-1] = 4$



26. **(d)** Pentagonal bipyramidal shape.

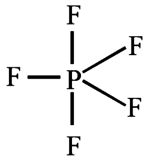


27. **(b)** Compounds involved in chelation become non-polar. Consequently such compounds are soluble in non-polar solvents like ether, benzene etc. and are only sparingly soluble in water whereas meta and para isomers are more soluble in water & less soluble in non-polar solvents.

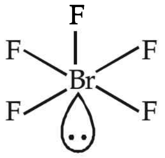


intra-molecular H-bonding

28. **(c)** PF_5 trigonal bipyramidal



BrF_5 square pyramidal (distorted)



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

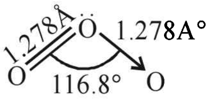
$$N_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2$$

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

both N_2 and C_2 have paired electrons in its molecular orbital hence are diamagnetic.

30. **(a)**

(a) $$\left.\begin{array}{l} ONCl = 8+7+17 = 32e^- \\ ONO^- = 8+7+8+1 = 24e^- \end{array}\right\}\text{not isoelectronic}$$

(b) 

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

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

(d) It is diamagnic in nature due to presence of paired electrons.

31. **(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 $He_2 = \frac{1}{2}(2-2) = 0$

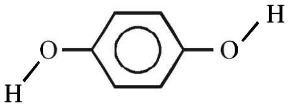
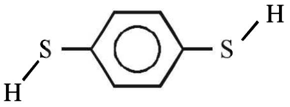
so both H_2^{2+} and He_2 does not exist

32. **(b)** $Li_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2$, $\therefore$ Bond order $= \frac{1}{2}(4-2) = 1$

$Li_2^+ = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^1$, B.O. $= \frac{1}{2}(3-2) = 0.5$

$Li_2^- = \sigma 1s^2\, \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^1$, B.O. $= \frac{1}{2}(4-3) = 0.5$

The bond order of Li_2^+ and Li_2^- is same but Li_2^+ is more stable than Li_2^- because Li_2^+ is smaller in size and has 2 electrons in Anti bonding orbital whereas Li_2^- has 3 electrons in Anti bonding orbital. hence Li_2^+ is more stable than Li_2^-

33. **(d)**  

In both the molecules the bond moments are not canceling with each other and hence the molecules has a resultant dipole and hence the molecule is polar.

34. **(c)** Hybridization (H) $= \frac{1}{2}$[no. of valence electrons of central atom + no. of Monovalent atoms attached to it + (–ve charge if any) – (+ve charge if any)]

$NO_2^+ = \frac{1}{2}[5+0+0-1] = 2$ i.e. sp hybridisation

$NO_2^- = \frac{1}{2}[5+0+1-0] = 3$ i.e. sp^2 hybridisation

$NO_3^- = \frac{1}{2}[5+0+1-0] = 3$ 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