

4



Chemical Bonding and Molecular Structure

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Isostructural species are those which have the same shape and hybridisation. Among the given species identify the isostructural pairs.

- (i) $[\text{NF}_3]$ and $[\text{BF}_3]$ (ii) $[\text{BF}_4^-]$ and $[\text{NH}_4^+]$
 (iii) $[\text{BCl}_3]$ and $[\text{BrCl}_3]$ (iv) $[\text{NH}_3]$ and $[\text{NO}_3^-]$

Ans. (ii)

Explanation: Both the molecules have sp^3 hybridisation and shape is tetrahedral.

2. Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?

- (i) CO_2 (ii) HI
 (iii) H_2O (iv) SO_2

Ans. (iii)

Explanation: Oxygen is highly electronegative and because of two lone pair on oxygen, the dipole moment is high.

3. The types of hybrid orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ respectively are expected to be

- (i) sp , sp^3 and sp^2 (ii) sp , sp^2 and sp^3
 (iii) sp^2 , sp and sp^3 (iv) sp^2 , sp^3 and sp

Ans. (ii)

Explanation: The hybridization in NO_2^+ is sp and in NO_3^- , sp^2 and in NH_4^+ , it is sp^3 .

4. Hydrogen bonds are formed in many compounds e.g., H_2O , HF, NH_3 . The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of above compounds is:

- (i) $\text{HF} > \text{H}_2\text{O} > \text{NH}_3$ (ii) $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$
 (iii) $\text{NH}_3 > \text{HF} > \text{H}_2\text{O}$ (iv) $\text{NH}_3 > \text{H}_2\text{O} > \text{HF}$

Ans. (ii)

Explanation: Strength of hydrogen bond depends on electronegativity, size of atom and number of hydrogen bonds per mol. F is most electronegative but, in H_2O , the no. of H-Bonds are more and size is smaller than N.

5. In PO_4^- ion the formal charge on the oxygen atom of P-O bond is

- (i) +1 (ii) -1
 (iii) -0.75 (iv) +0.75

Ans. (iii)

Explanation: The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence

electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure.

$$\boxed{\text{Formal charge (F.C.) on an atom in a Lewis structure}} = \boxed{\text{total number of valence electrons in the free atom}} - \boxed{\text{total number of non bonding (lone pair) electrons}} - \frac{1}{2} \boxed{\text{total number of bonding (shared) electrons}}$$

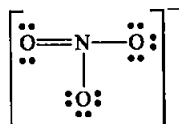
Formal charge on each O-atom = $\frac{\text{Total charge}}{\text{No. of O-atom}} = \frac{-3}{4} = -0.75$

6. In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are

- (i) 2, 2 (ii) 3, 1
 (iii) 1, 3 (iv) 4, 0

Ans. (iv)

Explanation: Central atom N is surrounded by 2 covalent bonds with 1 oxygen atom and 2 coordinate covalent bonds with 2 oxygen atoms.



7. Which of the following species has tetrahedral geometry?

- (i) BH_4^- (ii) NH_2^-
 (iii) CO_3^{2-} (iv) H_3O^+

Ans. (i)

Explanation: Boron is surrounded by 4 bonded pairs only.

In BH_4^- = no. of bond pair = 4

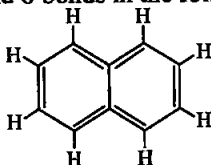
no. of lone pair = 0

sp^3 hybridised, so have tetrahedral geometry

NH_2^- = V-shape H_3O^+ = Pyramidal

CO_3^{2-} = triangular planar

8. Number of π bonds and σ bonds in the following structure is—



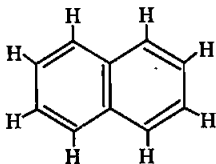
- (i) 6, 19 (ii) 4, 20
 (iii) 5, 19 (iv) 5, 20

Ans. (iii)

Explanation: Each C atom is sp^2 hybridized and surrounded by 3 sigma and 1 pi bond between two C atoms. Structure to be rectified.

$8\text{C}-\text{H} + 11\text{C}-\text{C}$ bonds = 19 σ bonds.

There are 5 π -bonds and 19 σ bonds.



9. Which molecule/ion out of the following does not contain unpaired electrons?

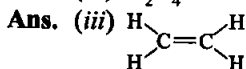
- (i) N_2^+ (ii) O_2
 (iii) O_2^{2-} (iv) B_2

Ans. (iii)

Explanation: In O_2^{2-} antibonding $P_{\pi} = P_{\pi^*}$ orbitals have paired electrons.

10. In which of the following molecule/ion all the bonds are not equal?

- (i) XeF_4 (ii) BF_4^-
 (iii) C_2H_4 (iv) SiF_4



Explanation: Each C atom is surrounded by 3 σ bonds and 1 π bond.

11. In which of the following substances will hydrogen bond be strongest?

- (i) HCl (ii) H_2O
 (iii) HI (iv) H_2S

Ans. (ii)

Explanation: Oxygen is more electronegative as compared to others and its size is small.

12. If the electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$, the four electrons involved in chemical bond formation will be _____.

- (i) $3p^6$ (ii) $3p^6, 4s^2$
 (iii) $3p^6, 3d^2$ (iv) $3d^2, 4s^2$

Ans. (iv)

Explanation: In bonding, valence electrons and electrons from penultimate shell participate. In transition elements ns electrons and $(n-1)d$ electrons participate.

13. Which of the following angle corresponds to sp^2 hybridisation?

- (i) 90° (ii) 120°
 (iii) 180° (iv) 109°

Ans. (ii)

Explanation: As a result of sp^2 hybridization geometry is triangular planar forming an angle of 120° with each other.

The electronic configurations of three elements, A, B and C are given below. Answer the questions 14 to 17 on the basis of these configurations.

A	$1s^2$	$2s^2$	$2p^6$		
B	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^3$
C	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$

14. Stable form of A may be represented by the formula:

- (i) A (ii) A_2
 (iii) A_3 (iv) A_4

Ans. (i)

Explanation: Octate of A is complete.

15. Stable form of C may be represented by the formula:

- (i) C (ii) C_2
 (iii) C_3 (iv) C_4

Ans. (ii)

Explanation: KK $[\sigma 2s]^2 [\sigma^* 2s]^2 [\pi 2p_x]^2 [\pi 2p_y]^2$

Bond order = $1/2 [6 - 2] = 2$

16. The molecular formula of the compound formed from B and C will be

- (i) BC (ii) B₂C
(iii) BC₂ (iv) BC₃

Ans. (iv)

Explanation: B represents phosphorus (P) and C represents Chlorine (Cl). The compound formed is PCl₃ i.e., BC₃.

17. The bond between B and C will be

- (i) Ionic (ii) Covalent
(iii) Hydrogen (iv) Coordinate

Ans. (ii)

Explanation: Both B and C are non-metals so, the bond formed between them will be covalent.

18. Which of the following order of energies of molecular orbitals of N₂ is correct?

- (i) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(ii) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(iii) $(\pi 2p_y) < (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(iv) $(\pi 2p_y) > (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

Ans. (i)

Explanation: Molecules like B₂, C₂ & N₂ having 1 to 3 electrons in *p* orbital energy of $\sigma 2p$ molecular orbital is greater than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.

19. Which of the following statement is not correct from the view point of molecular orbital theory?

- (i) Be₂ is not a stable molecule.
(ii) He₂ is not stable but He⁺ is expected to exist.
(iii) Bond strength of N₂ is maximum amongst the homonuclear diatomic molecules belonging to the second period.
(iv) The order of energies of molecular orbitals in N₂ molecule is $\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

Ans. (iv)

Explanation: The energy of $\sigma 2p$ molecular orbital is greater than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.

20. Which of the following options represents the correct bond order?

- (i) $O_2^- > O_2 > O_2^+$ (ii) $O_2^- < O_2 < O_2^+$
(iii) $O_2^- > O_2 < O_2^+$ (iv) $O_2^- < O_2 > O_2^+$

Ans. (ii)

Explanation: N_b electrons > N_a electrons and also depends on bond order.

$$\text{B.O.} = \frac{1}{2}(N_b - N_a)$$

21. The electronic configuration of the outermost shell of the most electronegative element is

- (i) 2s² 2p⁵ (ii) 3s² 3p⁵
(iii) 4s² 4p⁵ (iv) 5s² 5p⁵

Ans. (i)

Explanation: Elements of Group 17 has $ns^2 np^5$ electronic configuration. The electronegativity decreases down the group. The elements of this group are most electronegative.

22. Amongst the following elements whose electronic configurations are given below, the one having the highest ionisation enthalpy is

- (i) $[\text{Ne}]3s^2 3p^1$ (ii) $[\text{Ne}]3s^2 3p^3$
 (iii) $[\text{Ne}]3s^2 3p^2$ (iv) $[\text{Ar}]3d^{10} 4s^2 4p^3$

Ans. (ii)

Explanation: Since half filled p -orbital is more stable as compared to partially filled orbital.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

In the following questions two or more options may be correct.

23. Which of the following have identical bond order?

- (i) CN^- (ii) NO^+
 (iii) O_2^- (iv) O_2^{2-}

Ans. (i) and (ii)

Explanation: In both the species number of electrons in $N_b =$ number of electrons in N_{ab} .

24. Which of the following attain the linear structure:

- (i) BeCl_2 (ii) NCO^+
 (iii) NO_2 (iv) CS_2

Ans. (i) and (iv)

Explanation: In both central atom is sp hybridized.

25. CO is isoelectronic with

- (i) NO^+ (ii) N_2
 (iii) SnCl_2 (iv) NO_2^-

Ans. (i) and (ii)

Explanation: In both the species the number of electrons are same but the number of protons are different.

26. Which of the following species have the same shape?

- (i) CO_2 (ii) CCl_4
 (iii) O_3 (iv) NO_2

Ans. (iii) and (iv)

Explanation: Central atom in both the species has same hybridized state and same geometry.

27. Which of the following statements are correct about CO_3^{2-} ?

- (i) The hybridisation of central atom is sp^3 .
 (ii) Its resonance structure has one C–O single bond and two C=O double bonds.
 (iii) The average formal charge on each oxygen atom is 0.67 units.
 (iv) All C–O bond lengths are equal.

Ans. (iii) and (iv)

Explanation: In resonating structures bonds are not fixed and therefore, all bond lengths are equal.

28. Dimagnetic species are those which contain no unpaired electrons. Which among the following are dimagnetic?

- (i) N_2 (ii) N_2^{2-}
 (iii) O_2 (iv) O_2^{2-}

Ans. (i) and (iv)

Explanation: In both the species all orbitals have paired electrons.

29. Species having same bond order are :

- (i) N_2 (ii) N_2^-
 (iii) F_2^+ (iv) O_2^-

Ans. (iii) and (iv)

Explanation: In both the species number of electrons in bonding molecular orbital and in antibonding orbital are same.

30. Which of the following statements are not correct?

- (i) NaCl being an ionic compound is a good conductor of electricity in the solid state.
 (ii) In canonical structures there is a difference in the arrangement of atoms.
 (iii) Hybrid orbitals form stronger bonds than pure orbitals.
 (iv) VSEPR Theory can explain the square planar geometry of XeF_4 .

Ans. (i) and (ii)

Explanation: In first statement ions are not free in solid state but they are strongly bonded through electrostatic forces and second statement it does not show canonical structures being ionic compounds.

III. SHORT ANSWER TYPE

31. Explain the non linear shape of H_2S and non planar shape of PCl_3 using valence shell electron pair repulsion theory.

Ans. In both H_2S and PCl_3 , lone pairs are present along with bond pairs around the central atom. According to VSEPR, theory $L.P—L.P > L.P—B.P > B.P—B.P$. Therefore, shapes are different.

32. Using molecular orbital theory, compare the bond energy and magnetic character of O_2^+ and O_2^- species.

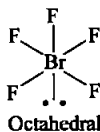
Ans. In O_2^+ , $B.O. = (10 - 5) / 2 = 2.5$

In O_2^- , $B.O. = (10 - 7) / 2 = 1.5$

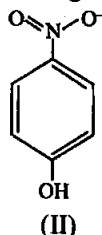
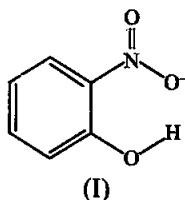
Bond dissociation energy is directly proportional to bond order and paramagnetic character depends on unpaired electrons. O_2^+ has high dissociation energy and both are paramagnetic.

33. Explain the shape of BrF_5 .

Ans. BrF_5 : Br is surrounded by 5 bonded pairs and one lone pair. Shape is square pyramidal.



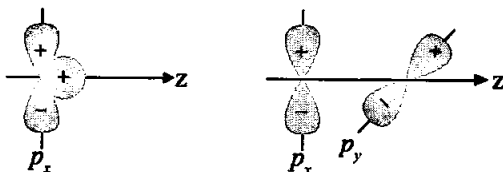
34. Structures of molecules of two compounds are given below:



- (a) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding.
- (b) The melting point of a compound depends on, among other things, the extent of hydrogen bonding. On this basis explain which of the above two compounds will show higher melting point.
- (c) Solubility of compounds in water depends on power to form hydrogen bonds with water. Which of the above compounds will form hydrogen bond with water easily and be more soluble in it.

- Ans.**
- (a) Compound (I) will form intramolecular hydrogen bonding because, NO_2 and OH groups are close together in comparison to that in compound (II).
 - (b) Compound (II) will have higher melting point because, it forms intermolecular H-bonds. Thus, more and more molecules are joined together through H-bonds.
 - (c) Due to intramolecular H-bonding, compound (I) will not be able to form hydrogen bonds with water thus, will be less soluble in it while compound (II) can form H-bond with water more easily and will be soluble in water.

35. Why does type of overlap given in the following figure not result in bond formation?



Ans. Same charges repel and there is zero overlapping hence, no bond formation.

36. Explain why PCl_5 is trigonal bipyramidal whereas IF_3 is square pyramidal.

Ans. In PCl_5 , P is surrounded by 5 bond pairs and no lone pairs, whereas in IF_3 , iodine atom is surrounded by 5 bond pairs and one lone pair, therefore the shape is different.

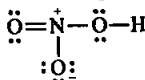
37. In both water and dimethyl ether ($\text{CH}_3-\ddot{\text{O}}-\text{CH}_3$), oxygen atom is central atom, and has the same hybridisation, yet they have different bond angles. Which one has greater bond angle? Give reason.

Ans. Dimethyl ether will have larger bond angle. Because of more repulsion between bond pairs of CH_3 groups attached in ether than between bond pairs of hydrogen atoms attached to oxygen in water. The carbon of CH_3 in ether is attached to three hydrogen atoms through bonds and electron pairs of these bonds add to the electronic charge density on carbon atom. Hence, repulsion between two $-\text{CH}_3$ groups will be more than that between two hydrogen atoms.

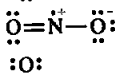
38. Write Lewis structure of the following compounds and show formal charge on each atom.



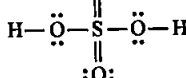
Ans. HNO_3 :



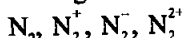
NO_2 :



H_2SO_4 :



39. The energy of $\sigma 2p_z$ molecular orbital is greater than $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals in nitrogen molecule. Write the complete sequence of energy levels in the increasing order of energy in the molecule. Compare the relative stability and the magnetic behaviour of the following species:



Ans. Configuration of N_2 : $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < [\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2 < [\pi^* 2p_x^2 = \pi^* 2p_y^2] < \sigma^* 2p_z^2$

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

N_2 is Diamagnetic, as all orbitals have paired electrons.

N_2^+ : $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < [\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2 < [\pi^* 2p_x^2 = \pi^* 2p_y^2] < \sigma^* 2p_z^1$

B.O. of $\text{N}_2^+ = (9 - 4)/2 = 2.5$

N_2^+ is Paramagnetic, as one of the orbitals has unpaired electron.

N_2^- : $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < [\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2 < [\pi^* 2p_x^2 = \pi^* 2p_y^2] < \sigma^* 2p_z^1$

B.O. of $\text{N}_2^- = (9 - 5)/2 = 2.5$

N_2^- is Paramagnetic, as one of the orbitals has unpaired electron.

N_2^{2+} : $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < [\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2 < [\pi^* 2p_x^1 = \pi^* 2p_y^1] < \sigma^* 2p_z^1$

B.O. of $\text{N}_2^{2+} = (8 - 4)/2 = 2$

It is Paramagnetic as two, of the orbitals have unpaired electron.

Stability: Stability of species depends on bond order and also depends on number of electrons present in bonding molecular orbital.

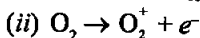
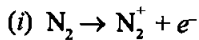
Increasing order of stability: $\text{N}_2^{2+} < \text{N}_2^- < \text{N}_2^+ < \text{N}_2$

N_2^{2+} = B.O. is lowest.

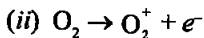
N_2^- and N_2^+ B.O. is same but number of electrons in bonding and in antibonding molecular orbitals are different. In N_2^- , in antibonding molecular orbitals, electrons are more than N_2^+ .

$N_2 =$ B.O. is higher.

40. What is the effect of the following processes on the bond order in N_2 and O_2 ?



Ans. (i) $N_2 \rightarrow N_2^+ + e^-$ [Bond order of N_2 is 3 while of N_2^+ is 2.5]
Bond order decreases.



[Bond order of O_2 is 2 while of O_2^+ is 2.5]

Bond order increases.

41. Give reasons for the following:

(i) Covalent bonds are directional bonds while ionic bonds are non-directional.

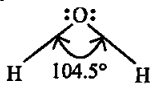
(ii) Water molecule has bent structure whereas carbon dioxide molecule is linear.

(iii) Ethyne molecule is linear.

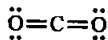
Ans. (i) A covalent bond is a directional bond because it is formed by the overlapping of atomic orbitals. Ionic bond is non directional because it is formed by the transference of electrons and electrostatic field of an ion is there which is non directional. Positive ion is surrounded by number of anions in any direction depending upon the size and vice-versa.

(ii) In H_2O , oxygen atom is sp^3 hybridized and surrounded by two lone pairs and two bonded pairs. The four sp^3 hybrid orbitals give distorted tetrahedral geometry in which the two corners are occupied by hydrogen atoms while other two by the lone pairs.

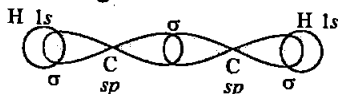
The bond angle is reduced to 104.5° from 109.5° due to greater repulsive forces between $lp - lp$ and molecule acquires a bent or V-shaped structure.



In CO_2 , carbon atom is sp hybridized and two sp hybrid orbitals are oriented in opposite direction forming linear shape with an angle of 180° .



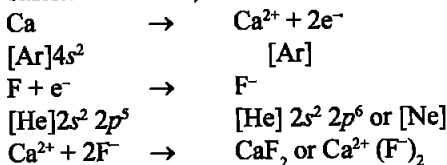
(iii) In ethyne molecule, both the carbon atoms are sp hybridized and two unhybridized orbitals. Hybridized orbitals of both the carbon atoms are oriented in opposite directions forming a linear structure with an angle of 180° .



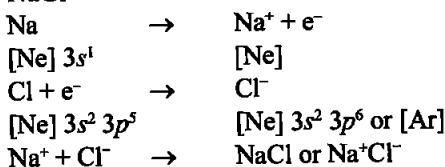
42. What is an ionic bond? With two suitable examples explain the difference between an ionic and a covalent bond?

Ans. Ionic bond: The bond which is formed by the complete transference of electrons from one atom to other atom as a result positive and negative ions are formed. These ions are held together through electrostatic force of attraction. This force of attraction is called ionic bond, e.g.,

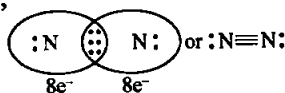
The formation of calcium fluoride,



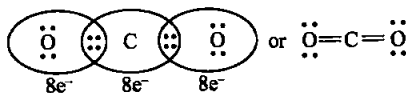
The formation of NaCl



Covalent bond: The bond which is formed between the two atoms of non-metals by mutual sharing of electrons between them is called covalent bond, e.g.,

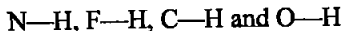


Covalent bond between two N atoms.

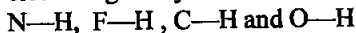


Double bonds in CO_2 molecule.

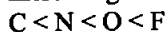
43. Arrange the following bonds in order of increasing ionic character giving reason.



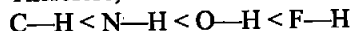
Ans. Ionic character of the bond depends on the difference of electronegativity. It is directly proportional to difference of electronegativity. In the following bonds hydrogen is in all but other atoms have different electronegativity.



Increasing order of electronegativity is:

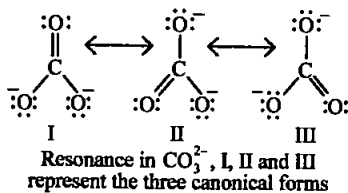


Therefore, ionic character of the bond (Increasing order)

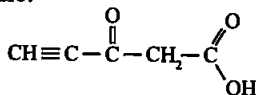


44. Explain why CO_3^{2-} ion cannot be represented by a single Lewis structure. How can it be best represented?

Ans. In CO_3^{2-} ion, there are three C—O bonds and all have same bond length because it shows resonating structures not only one structure. Lewis structures explain all the properties.



45. Predict the hybridisation of each carbon in the molecule of organic compound given below. Also indicate the total number of sigma and pi bonds in this molecule.



Ans. In the given structure, there are total 5 carbon atoms, two carbon atoms are sp hybridized and linked through triple bond, two carbon atoms are sp^2 hybridized and linked through double bonds to O atoms and one is sp^3 hybridized that is linked to two C atoms through single bonds and to two H atoms through single bonds.

In the molecule, there are 11σ bonds and 4π bonds.

46. Group the following as linear and non-linear molecules:



Ans. Only BeCl_2 is linear because in all others, central atom O is surrounded by two lone pairs. Due to $lp-lp$ repulsion, molecules are non-linear.



47. Elements X, Y and Z have 4, 5 and 7 valence electrons respectively.

(i) Write the molecular formula of the compounds formed by these elements individually with hydrogen.

(ii) Which of these compounds will have the highest dipole moment?

Ans. (i) The molecular formula of the compounds formed by X, Y and Z with hydrogen are XH_4 , YH_3 and $\text{H}-\text{Z}$.

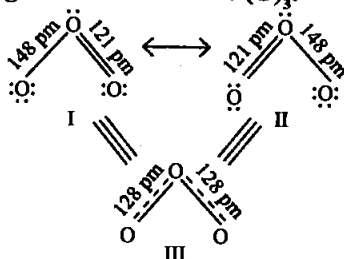
(ii) X, Y and Z have 4, 5 and 7 electrons respectively. These elements belong to 2nd period and 14th, 15th and 17th groups. Electronegativity of elements increases across the period from group 1 to group 17. Hence, $\text{H}-\text{Z}$ will have the highest dipole moment.

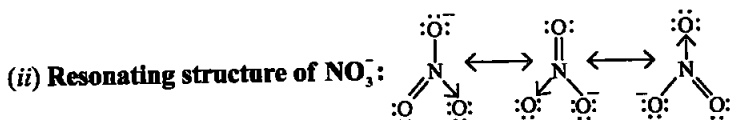
48. Draw the resonating structure of

(i) Ozone molecule

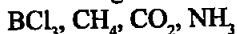
(ii) Nitrate ion

Ans. (i) Resonating structure of Ozone (O_3):

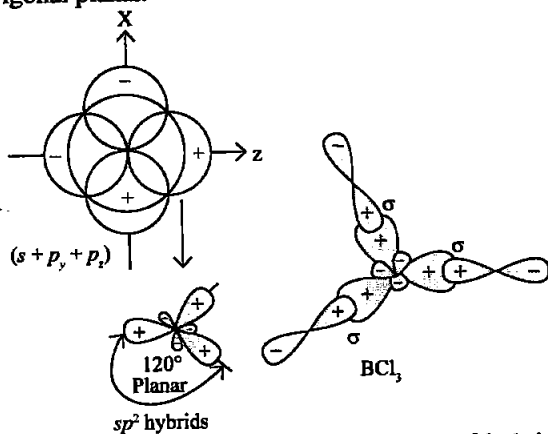




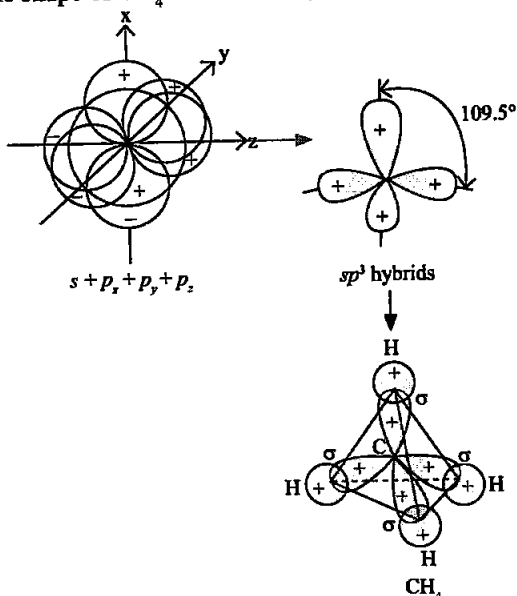
49. Predict the shapes of the following molecules on the basis of hybridisation.



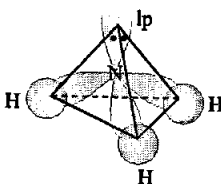
Ans. (i) In BCl_3 , Boron is sp^2 hybridized and thus, the shape of BCl_3 is trigonal planar.



(ii) The shape of CH_4 is tetrahedral, carbon is sp^3 hybridized.

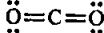


(iii) The shape of NH_3 molecule is pyramidal, nitrogen atom is sp^3 hybridized but lone pair on N gives pyramidal shape.



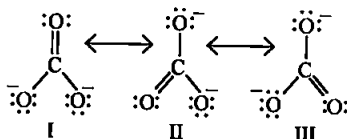
Ammonia, NH_3

(iv) CO_2 is linear because carbon is sp hybridized.



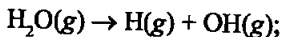
50. All the C—O bonds in carbonate ion (CO_3^{2-}) are equal in length. Explain.

Ans. In CO_3^{2-} ion, carbon is bonded to three oxygen atoms. It is bonded to two oxygen atoms by double bonds and one with single bond. Bonds are not fixed and show resonance therefore, all C—O bonds are equal in length.

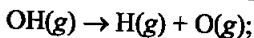


51. What is meant by the term average bond enthalpy? Why is there difference in bond enthalpy of O—H bond in ethanol ($\text{C}_2\text{H}_5\text{OH}$) and water?

Ans. Average bond enthalpy is obtained by dividing total bond dissociation enthalpy by the number of bonds broken. All the identical bonds in a molecule do not have the same bond enthalpies, e.g., in water (H_2O), there are two O—H bonds but breaking of first O—H bond, the second O—H bond undergoes some change because of charge. Therefore, in polyatomic molecules average bond enthalpy is used and calculated by dividing total bond dissociation enthalpy by the number of bonds broken.



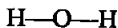
$$\Delta_a H_1^\ominus = 502 \text{ kJ mol}^{-1}$$



$$\Delta_b H_2^\ominus = 427 \text{ kJ mol}^{-1}$$

$$\text{Average O—H bond enthalpy} = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

The bond enthalpies of O—H in $\text{C}_2\text{H}_5\text{OH}$ and H_2O are different because of different electronic environment around oxygen atom.



In ethanol, —OH is attached to carbon and in water O—H is attached to hydrogen atom.

IV. MATCHING TYPE

52. Match the species in Column I with the type of hybrid orbitals in Column II.

Column I	Column II
(i) SF_4	(a) sp^3d^2
(ii) IF_5	(b) d^2sp^3

(iii) NO_2^+	(c) sp^3d
(iv) NH_4^+	(d) sp^3
	(e) sp

Ans. (i) \rightarrow (c); (ii) \rightarrow (a); (iii) \rightarrow (e); (iv) \rightarrow (d)

Explanation:

Column I	Column II
(i) SF_4	S is surrounded by 4 bond pairs and 1 lone pair (sp^3d hybridization).
(ii) IF_5	I is surrounded by 5 bond pairs and 1 lone pair (sp^3d^2 hybridization).
(iii) NO_2^+	N has 2 bond pairs and no lone pair (sp hybridization).
(iv) NH_4^+	N has 4 bond pairs and no lone pair (sp^3 hybridization).

53. Match the species in Column I with the geometry/shape in Column II.

Column I	Column II
(i) H_3O^+	(a) Linear
(ii) $\text{HC} \equiv \text{CH}$	(b) Angular
(iii) ClO_2^-	(c) Tetrahedral
(iv) NH_4^+	(d) Trigonal bipyramidal
	(e) Pyramidal

Ans. (i) \rightarrow (e); (ii) \rightarrow (a); (iii) \rightarrow (b); (iv) \rightarrow (c)

Explanation:

Column I	Column II
(i) H_3O^+	Oxygen has 3 bond pairs and 1 lone pair (pyramidal shape).
(ii) $\text{HC} \equiv \text{CH}$	linear as sp hybridized.
(iii) ClO_2^-	Cl has 2 bond pairs and 2 lone pairs (Angular shape).
(iv) NH_4^+	N has 4 bond pairs and no lone pair (Tetrahedral).

54. Match the species in Column I with the bond order in Column II.

Column I	Column II
(i) NO	(a) 1.5
(ii) CO	(b) 2.0
(iii) O_2^-	(c) 2.5
(iv) O_2	(d) 3.0

Ans. (i) → (c); (ii) → (d); (iii) → (a); (iv) → (b)

Explanation:

Column I	Column II
(i) NO	NO (7 + 8 = 15 electrons) $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < [\pi 2p_x^2 = \pi 2p_y^2]$ $< [\pi^* 2p_x^1 = \pi^* 2p_y^1] < \sigma^* 2p_z$ Bond order = $(N_b - N_a)/2 = *(10 - 5)/2 = 2.5$
(ii) CO	CO (6 + 8 = 14 electrons) $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < [\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2$ $< [\pi^* 2p_x^1 = \pi^* 2p_y^1] < \sigma^* 2p_z$ Bond order = $(N_b - N_a)/2 = (10 - 4)/2 = 3$
(iii) O_2^-	(8 + 8 + 1 = 17 electrons) $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < [\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2 < [\pi^* 2p_x^2 = \pi^* 2p_y^1] < \sigma^* 2p_z$ Bond order = $(N_b - N_a)/2 = (10 - 7)/2 = 1.5$
(iv) O_2	(8 + 8 = 16 electrons) $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < [\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2 < [\pi^* 2p_x^1 = \pi^* 2p_y^1] < \sigma^* 2p_z$ Bond order = $(N_b - N_a)/2 = (10 - 6)/2 = 2$

55. Match the items given in Column I with examples given in Column II.

Column I	Column II
(i) Hydrogen bond	(a) C
(ii) Resonance	(b) LiF
(iii) Ionic solid	(c) H_2
(iv) Covalent solid	(d) HF
	(e) O_3

Ans. (i) → (d); (ii) → (e); (iii) → (b); (iv) → (a)

56. Match the shape of molecules in Column I with the type of hybridisation in Column II.

Column I	Column II
(i) Tetrahedral	(a) sp^2
(ii) Trigonal	(b) sp
(iii) Linear	(c) sp^3

Ans. (i) → (c); (ii) → (a); (iii) → (b)

V. ASSERTION AND REASON TYPE

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

57. Assertion (A) : Sodium chloride formed by the action of chlorine gas on sodium metal is a stable compound.

Reason (R) : This is because sodium and chloride ions acquire octet in sodium chloride formation.

- (i) A and R both are correct, and R is the correct explanation of A.
- (ii) A and R both are correct, but R is not the correct explanation of A.
- (iii) A is true but R is false.
- (iv) A and R both are false.

Ans. (i)

Explanation: $\text{Na} + \text{Cl} \rightarrow \text{NaCl}$
 2,8,1 2,8,7 (2,8)(2,8,8)

In NaCl, Sodium and Chloride ions have complete octet hence, NaCl is stable compound.

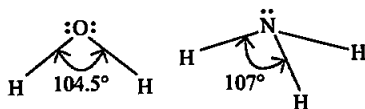
58. Assertion (A) : Though the central atom of both NH_3 and H_2O molecules are sp^3 hybridised, yet H–N–H bond angle is greater than that of H–O–H.

Reason (R) : This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.

- (i) A and R both are correct, and R is the correct explanation of A.
- (ii) A and R both are correct, but R is not the correct explanation of A.
- (iii) A is true but R is false.
- (iv) A and R both are false.

Ans. (i)

Explanation:



59. Assertion (A) : Among the two O–H bonds in H_2O molecule, the energy required to break the first O–H bond and the other O–H bond is the same.

Reason (R) : This is because the electronic environment around oxygen is the same even after breakage of one O–H bond.

- (i) A and R both are correct, and R is correct explanation of A.
- (ii) A and R both are correct, but R is not the correct explanation of A.
- (iii) A is true but R is false.
- (iv) A and R both are false.

Ans. (iv)

Explanation: Correct assertion : The bond enthalpy in H–O–H is not same for both the O–H bonds.

Correct reason : Because electronic charge on oxygen atom is different after breaking of one O–H bond.

VI. LONG ANSWER TYPE

60. (i) Discuss the significance/applications of dipole moment.
 (ii) Represent diagrammatically the bond moments and the resultant dipole moment in CO_2 , NF_3 and CHCl_3 .

Ans. (i) **Applications of dipole moment:**

Dipole moment (μ) = charge (Q) \times distance of separation (r)

Dipole moment is usually expressed in Debye units (D).

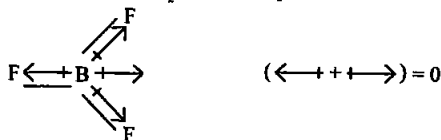
(a) It helps to predict polar and non-polar nature of compounds

(b) The percentage of ionic character can be calculated:

$$\% \text{ of ionic character} = \mu_{\text{observed}} \times 100 / \mu_{\text{ionic}}$$

(c) It helps to know the symmetry of molecule. Symmetrical molecules have zero dipole moment, although they have two or more polar bonds. For example,

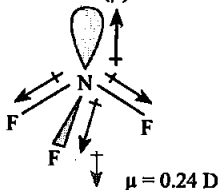
The dipole moment in case of BeF_2 is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.



(a) BF_3 molecule; representation of
 (a) bond dipoles and (b) total dipole moment

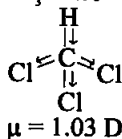
(ii) For CO_2 : $\text{O} \equiv \text{C} \equiv \text{O}$
 dipole moment (μ) = 0

For NF_3 :



Resultant dipole moment
 in $\text{NF}_3 = 0.80 \times 10^{-30} \text{ Cm}$

For CHCl_3 :



61. Use the molecular orbital energy level diagram to show that N_2 would be expected to have a triple bond, F_2 , a single bond and Ne_2 , no bond.

Ans. **Formation of N_2 molecule: Electronic Configuration**

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 [\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2$$

$$\text{Bond order} = (N_b - N_a)/2 = (10 - 4)/2 = 3$$

Bond order indicates the number of bonds in diatomic molecule. Triple bond $N \equiv N$.

Formation of F_2 molecule: Electronic Configuration

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma^* 2p_z^2 < [\pi 2p_x^2 = \pi 2p_y^2] < [\pi^* 2p_x^2 = \pi^* 2p_y^2] < \sigma^* 2p_z$$

$$\text{Bond order} = (N_b - N_a)/2 = (10 - 8)/2 = 1. \text{ Single bond } F-F.$$

Formation of Ne_2 molecule: Electronic Configuration

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < [\pi 2p_x^2 = \pi 2p_y^2] < [\pi^* 2p_x^2 = \pi^* 2p_y^2] < \sigma^* 2p_z$$

$$\text{Bond order} = (N_b - N_a)/2 = (10 - 10)/2 = 0. \text{ No bond between Ne atoms.}$$

62. Briefly describe the valence bond theory of covalent bond formation by taking an example of hydrogen. How can you interpret energy changes taking place in the formation of dihydrogen?

Ans. Valence bond theory was introduced by Heitler and London in 1927 and developed by Pauling. It is based on the knowledge of atomic orbitals, electronic configurations of elements, overlapping of atomic orbitals and hybridization of orbitals.

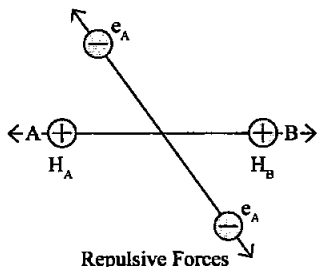
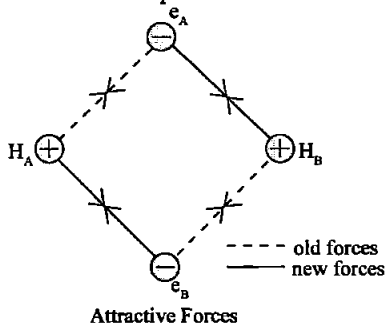
Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B . When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate. Attractive forces arise between:

- (i) Nucleus of one atom and its own electron that is $N_A - e_A$ and $N_B - e_B$.
- (ii) Nucleus of one atom and electron of other atom *i.e.*, $N_A - e_B$, $N_B - e_A$.

Similarly, repulsive forces arise between

- (a) electrons of two atoms like $e_A - e_B$,
- (b) nuclei of two atoms $N_A - N_B$.

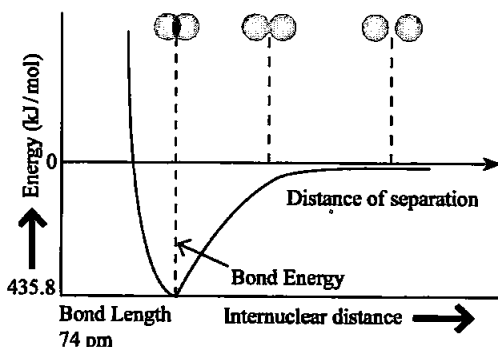
Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart.



Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms

approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

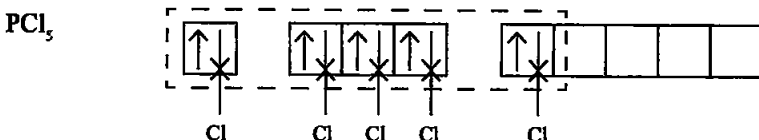
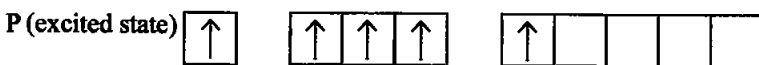
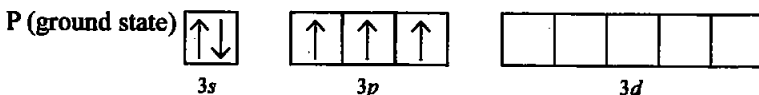
Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as **bond enthalpy**, which is corresponding to minimum in the curve depicted in figure. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule. $H_2(g) + 435.8 \text{ kJ mol}^{-1} \rightarrow H(g) + H(g)$.



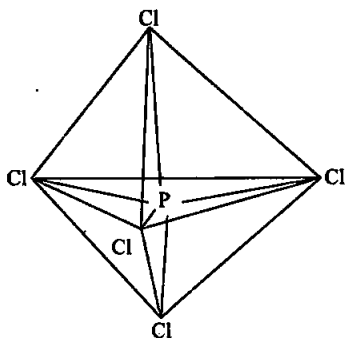
The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2 .

63. Describe hybridisation in the case of PCl_5 and SF_6 . The axial bonds are longer as compared to equatorial bonds in PCl_5 , whereas in SF_6 both axial bonds and equatorial bonds have the same bond length. Explain.

Ans. Formation of PCl_5 (sp^3d hybridization): The ground state and the excited state outer electronic configurations of phosphorus ($Z = 15$) are represented below:

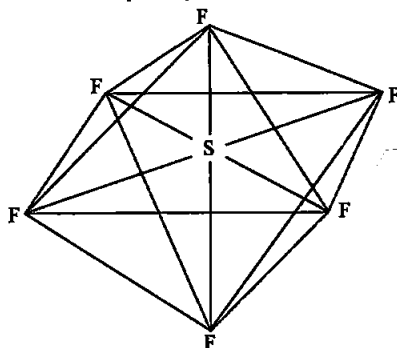
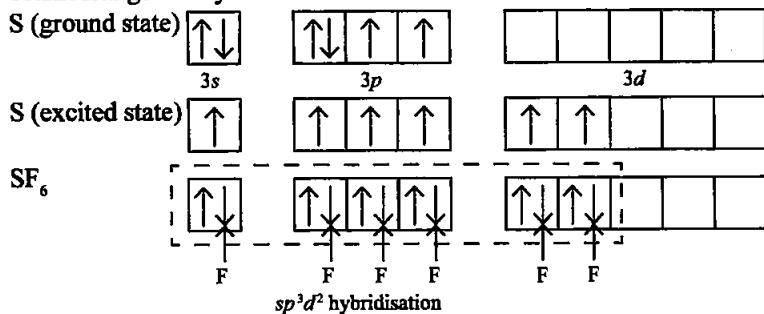


sp^3d hybrid orbitals filled by electron pairs donated by five Cl atoms.

Trigonal bipyramidal geometry of PCl_5 molecule

Three P—Cl bond lie in one plane and make an angle of 120° with each other; these bonds are termed as equatorial bonds. The remaining two P—Cl bonds—one lying above and the other lying below the equatorial plane, make an angle of 90° with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction than the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes PCl_5 molecule more reactive.

Formation of SF_6 (sp^3d^2 hybridization): Molecule has a regular octahedral geometry.

Octahedral geometry of SF_6 molecule

64. (i) Discuss the concept of hybridisation. What are its different types in a carbon atom.
- (ii) What is the type of hybridisation of carbon atoms marked with star.
- (a) $\text{CH}_2=\overset{\cdot}{\text{C}}\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$
- (b) $\text{CH}_3-\overset{\cdot}{\text{C}}\text{H}_2-\overset{\text{OH}}{\text{O}}$
- (c) $\text{CH}_3-\overset{\cdot}{\text{C}}\text{H}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$
- (d) $\text{CH}_3-\overset{\cdot}{\text{C}}\text{H}=\text{C}\text{H}-\overset{\cdot}{\text{C}}\text{H}_3$
- (e) $\text{CH}_3-\overset{\cdot}{\text{C}}\equiv\text{CH}$

Ans. (i) **Hybridisation:** In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4 , NH_3 and H_2O etc., Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals**. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape.

For example, when one $2s$ and three $2p$ -orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

The main features of hybridisation are as under:

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement.

Therefore, the type of hybridisation indicates the geometry of the molecules.

Different types of hybridisation in carbon atom are:

- In carbon compounds, if carbon is linked to carbon through triple bond ($\text{C}\equiv\text{C}$), e.g., Alkynes, triple bonded carbon is sp hybridised.
- In carbon compounds, if carbon is linked to carbon through double bond ($\text{C}=\text{C}$), e.g., Alkenes, double bonded carbon is sp^2 hybridised.
- In carbon compounds, if carbon is linked to carbon through single bond ($\text{C}-\text{C}$), e.g., Alkanes, single bonded carbon is sp^3 hybridised.

- (ii) (a) $\overset{\cdot}{\text{C}}\text{H}_2=\overset{\cdot}{\text{C}}\text{H}-\overset{\cdot}{\underset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{H}$
Both the starred C atoms are sp^2 hybridised.
- (b) $\text{CH}_3-\overset{\cdot}{\text{C}}\text{H}_2-\text{OH}$
The starred C atom is sp^3 hybridised.
- (c) $\text{CH}_3-\text{CH}_2-\overset{\cdot}{\underset{\text{O}}{\parallel}}{\text{C}}-\text{H}$
The starred C atom is sp^2 hybridised.
- (d) $\overset{\cdot}{\text{C}}\text{H}_3-\text{CH}=\overset{\cdot}{\text{C}}\text{H}-\text{CH}_3$
The starred C atom is sp^3 hybridised.
- (e) $\text{CH}_3-\overset{\cdot}{\text{C}}\equiv\text{CH}$
The starred C atom is sp^2 hybridised.

Comprehension given below is followed by some multiple choice questions. Each question has one correct option. Choose the correct option. (65-68)

Molecular orbitals are formed by the overlap of atomic orbitals. Two atomic orbitals combine to form two molecular orbitals called bonding molecular orbital (BMO) and anti bonding molecular orbital (ABMO). Energy of anti bonding orbital is raised above the parent atomic orbitals that have combined and the energy of the bonding orbital is lowered than the parent atomic orbitals. Energies of various molecular orbitals for elements hydrogen to nitrogen increase in the order:

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x \approx \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$ and for oxygen and fluorine order of energy of molecular orbitals is given below:

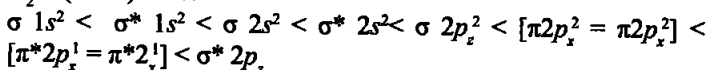
$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x \approx \pi 2p_y) < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$

Different atomic orbitals of one atom combine with those atomic orbitals of the second atom which have comparable energies and proper orientation. Further, if the overlapping is head on, the molecular orbital is called 'Sigma', (σ), and if the overlap is lateral, the molecular orbital is called 'pi', (π). The molecular orbitals are filled with electrons according to the same rules as followed for filling of atomic orbitals. However, the order for filling is not the same for all molecules or their ions. Bond order is one of the most important parameters to compare the strength of bonds.

65. Which of the following statements is correct?

- In the formation of dioxygen from oxygen atoms 10 molecular orbitals will be formed.
- All the molecular orbitals in the dioxygen will be completely filled.
- Total number of bonding molecular orbitals will not be same as total number of anti bonding orbitals in dioxygen.
- Number of filled bonding orbitals will be same as number of filled anti bonding orbitals.

Ans. (i) $O_2 = (8 + 8) = 16.$



66. Which of the following molecular orbitals has maximum number of nodal planes?

(i) $\sigma^* 1s$

(ii) $\sigma^* 2p_z$

(iii) $\pi 2p_x$

(iv) $\pi^* 2p_y$

Ans. (iv) $\pi^* 2p_y$ has 2 nodal planes and rest have 1 nodal plane.

67. Which of the following pair is expected to have the same bond order?

(i) O_2, N_2

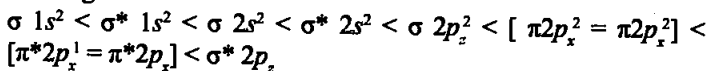
(ii) O_2^+, N_2^-

(iii) O_2^-, N_2^+

(iv) O_2^-, N_2^-

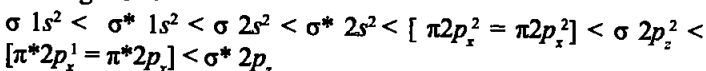
Ans. (ii) Bond order = $(N_b - N_a) / 2$

In O_2^+ , number of electrons in bonding orbitals are 10 and in antibonding are 5.



$$\text{Bond order} = (10 - 5) / 2 = 2.5$$

In N_2^- , number of electrons in bonding orbitals are 10 and in antibonding are 5.



$$\text{Bond order} = (10 - 5) / 2 = 2.5.$$

68. In which of the following molecules, $\sigma 2p_z$ molecular orbital is filled after $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals?

(i) O_2

(ii) Ne_2

(iii) N_2

(iv) F_2

Ans. (iii) $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < [\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2 < [\pi^* 2p_x^1 = \pi^* 2p_y^1] < \sigma^* 2p_z$

We have seen that 1s atomic orbitals on two atoms form two molecular orbitals designated as $\sigma 1s$ and $\sigma^* 1s$. In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals.

Antibonding MOs $\sigma^* 2s \sigma^* 2p_z \pi^* 2p_x \pi^* 2p_y$

Bonding MOs $\sigma 2s \sigma 2p_z \pi 2p_x \pi 2p_y$

It has been observed experimentally that for molecules such as B_2 , C_2 , N_2 etc, the increasing order of energies of various molecular orbitals is $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

The important characteristic feature of this order is that the energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.

□□□