4

Chemical Bonding and Molecular Structure

Multiple Choice Questions (MCQs)

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

(a) [NF_3 and BF_3]
(b) [BF_4^- and NH_4^+]
(c) [BCl_3 and $BrCl_3$]
(d) [NH_3 and NO_3^-]

Ans. *(b)*

(a) NF_3 is pyramidal whereas BF_3 is planar triangular.
(b) BF_4^- and NH_4^+ ion both are tetrahedral and sp^3 hybridisation.
(c) BCl_3 is triangular planar whereas $BrCl_3$ is *T* shaped.
(d) NH_3 is pyramidal whereas NO_3^- is triangular planar.

Q. 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?

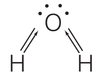
(a) CO_2
(b) HI
(c) H_2O
(d) SO_2

Ans. *(c)* CO_2 being symmetrical has zero dipole moment

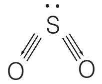
$$O\overset{\leftarrow}{=}C\overset{\leftarrow}{=}O$$
$$\mu = 0$$

Among HI, SO_2 and H_2O dipole moment is highest for H_2O as in it the central atom contains 2 lone pairs.

$$\overrightarrow{H - I}$$
$$\mu = 0.38D$$



$\mu = 1.84$ D



$\mu = 1.62$ D

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

(a) sp, sp^3 and sp^2
(b) sp, sp^2 and sp^3
(c) sp^2, sp and sp^3
(d) sp^2, sp^3 and sp

Ans. *(b)* The type of hybrid orbitals of nitrogen can be decided by using VSEPR theory counting *bp* and as *lp* in

$NO_2^+ = 2\ bp + 0\ lp$ = linear = sp hybridised

$NO_3^- = 3\ bp + 0\ lp \Rightarrow sp^2$ hybridised

$NH_4^+ = 4\ bp + 0\ lp \Rightarrow sp^3$ hybridised

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

(a) $HF > H_2O > NH_3$
(b) $H_2O > HF > NH_3$
(c) $NH_3 > HF > H_2O$
(d) $NH_3 > H_2O > HF$

Ans. *(b)* Strength of H-bond is in the order H....F >H.....O >H.....N.

But each H_2O molecule is linked to four other H_2O molecules through H-bonds whereas each HF molecule is linked only to two other HF molecules.

Hence, b.p of H_2O > b.p of HF > b.p. of NH_3

Q. 5 In PO_4^{3-} ion the formal charge on the oxygen atom of P—O bond is

(a) + 1
(b) − 1
(c) − 0.75
(d) + 0.75

Ans. *(c)* In PO_4^{3-} ion, formal charge on each O-atom of P—O bond

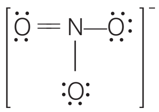
$$= \frac{\text{total charge}}{\text{Noumber of O-atom}} = -\frac{3}{4} = -0.75$$

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

(a) 2, 2
(b) 3, 1
(c) 1, 3
(d) 4, 0

Thinking Process

To solve this question, we must know the structure of NO_3^- *ion i.e.,*



Then, count the bond pairs and lone pairs of electron on nitrogen.

Ans. *(d)* In N-atom, number of valence electrons = 5

Due to the presence of one negative charge, number of valence electrons = 5 + 1 = 6 one O-atom forms two bond (= bond) and two O-atom shared with two electrons of N-atom

Thus, 3 O-atoms shared with 8 electrons of N-atom.

∴ Number of bond pairs (or shared pairs) = 4

Number of lone pairs = 0

Q. 7 Which of the following species has tetrahedral geometry?

(a) BH_4^- (b) NH_2^- (c) CO_3^{2-} (d) H_3O^+

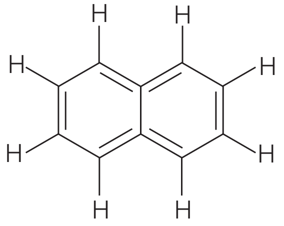
Ans. ***(a)*** $BH_4^- \Rightarrow$ 4 bond pairs + 0 lone pair $\Rightarrow sp^3$ hybridised = tetrahedral geometry

NH_2^- = V – shape

CO_3^{2-} = triangular planar

H_3O^+ = pyramidal

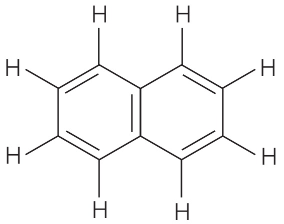
Q. 8 Number of π bonds and σ bonds in the following structure is



Biphenyl

(a) 6, 19 (b) 4, 20 (c) 5, 19 (d) 5, 20

Ans. ***(c)*** The given compound will have the correct structure as



There are 5 π-bonds and $8\,C—H + 11\,C—C$ σ-bonds, *i.e.,* 19 σ-bonds are present in the above molecule.

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

(a) N_2^+ (b) O_2 (c) O_2^{2-} (d) B_2

Ans. ***(c)*** The electronic configuration of the given molecules are

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

It has one unpaired electron.

$O_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^1$

O_2 has two unpaired electrons.

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

Thus, O_2^{2-} has no unpaired electrons.

$B_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 \approx \pi_2 p_y^1$

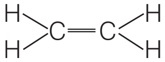
Thus, B_2 has two unpaired electrons.

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

(a) XeF_4 (b) BF_4^- (c) C_2H_4 (d) SiF_4

Ans. ***(c)*** $XeF_4 \Rightarrow 4\ bp + 2\ lp \Rightarrow$ square planar $\Rightarrow$ all bonds are equal

$BF_4^- \Rightarrow 4\ bp + 0\ lp \Rightarrow$ tetrahedral (all bonds are equal)

$C_2H_4 \Rightarrow$  $\Rightarrow$ C$=$C bond is not equal to C—H bond

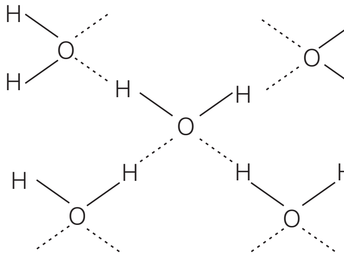
$SiF_4 \Rightarrow 4\ bp + 0\ lp \Rightarrow$ tetrahedral (all bonds are equal)

Thus, in C_2H_4 all the bonds are not equal.

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

(a) HCl (b) H_2O (c) HI (d) H_2S

Ans. ***(b)*** HCl, HI and H_2S do not from H-bonds. Only H_2O forms hydrogen bonds. One H_2O molecule forms four H-bonding.



Q. 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

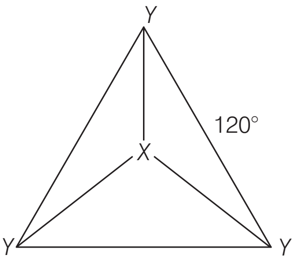
(a) $3p^6$ (b) $3p^6, 4s^2$ (c) $3p^6, 3d^2$ (d) $3d^2, 4s^2$

Ans. ***(d)*** The given electronic configuration shows that an element is vanadium ($Z=22$). It belongs to *d*-block of the periodic table. In transition elements *i.e.,* *d*-block elements, electrons of *ns* and $(n-1)\,d$ subshell take part in bond formation.

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

(a) 90° (b) 120° (c) 180° (d) 109°

Ans. ***(b)*** For sp^2 hybridisation, the geometry is generally triangular planar.



Thus, bond angle is 120°.

Direction (Q. Nos. 14-17) *The electronic configurations of the elements A, B and C are given below. Answer the questions from 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	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$

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

(a) A (b) A_2 (c) A_3 (d) A_4

Ans. ***(a)*** The given electronic configuration shows that A represents noble gas because the octet is complete. A is neon which has 10 atomic number.

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

(a) C (b) C_2 (c) C_3 (d) C_4

Ans. ***(b)*** The electronic configuration of C represent chlorine. Its stable form is dichlorine (Cl_2) *i.e.*, C_2.

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

(a) BC (b) B_2C (c) BC_2 (d) BC_3

Ans. ***(d)*** The electronic configuration show that B represents phosphorus and C represents chlorine. The stable compound formed is PCl_3 *i.e.*, BC_3.

Q. 17 The bond between B and C will be

(a) ionic (b) covalent (c) hydrogen (d) coordinate

Ans. ***(b)*** The bond between B and C will be covalent. Both B and C are non-metal atoms. B represents phosphorus and C represent chlorine.

Q. 18 Which of the following order of energies of molecular orbitals of N_2 is correct?

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

(b) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$

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

(d) $(\pi 2p_y) > (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

Ans. ***(a)*** The correct increasing order of energies of molecular orbitals of N_2 is given below

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

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

(a) Be_2 is not a stable molecule

(b) He_2 is not stable but He_2^+ is expected to exist.

(c) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.

(d) The order of energies of molecular orbitals in N_2 molecule is
$\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x \simeq \pi 2p_y) < (\pi^* 2p_x \simeq \pi^* 2p_y) < \sigma^* 2p_z$

Ans. ***(d)*** Existance of molecule, bonding nature and energy order of molecular orbitals can be explained on the basis of molecular orbital theory as follows

(i) Molecules having zero bond order never exists while molecular having non-zero bond order is either exists or expected to exist.

(ii) Higher the value of bond order, higher will be its bond strength.

Electrons present in bonding molecular orbital are known as bonding electrons (N_b) and electrons present on anti-bonding molecular orbital are known as anti-bonding electrons (N_a) and half of their difference is known as bond order *i.e.,*

(a) Be_2 $(4 + 4 = 8) = \sigma 1s^2, \sigma^* 1s^2, \sigma 1s^2, \sigma^* 2s^2$

$$\text{Bond order (BO)} = \frac{1}{2}$$

[Number of bonding electrons (N_b) – Number of anti-bonding electrons N_a]

$$= \frac{4-4}{2} = 0$$

Here, bond order of Be_2 is zero. Thus, it does not exist.

(b) He_2 $(2 + 2 = 4) = \sigma 1s^2, \sigma^* 1s^2$

$$BO = \frac{2-2}{2} = 0$$

Here, bond order of Be_2 is zero. Hence, it does not exist.

$$He_2^+ \ (2 + 2 - 1 = 3) = \sigma 1s^2, \sigma^* 1s^1$$

$$BO = \frac{2-1}{2} = 0.5$$

Since, the bond order is not zero, this molecule is expected to exist.

(c) N_2 $(7 + 7 = 14) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_X^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

$$BO = \frac{10-4}{2} = 3$$

Thus, dinitrogen (N_2) molecule contain triple bond and no any molecule of second period have more than double bond. Hence, bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.

(d) It is incorrect. The correct order of energies of molecular orbitals in N_2 molecule is

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

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

(a) $O_2^- > O_2 > O_2^+$ (b) $O_2^- < O_2 < O_2^+$ (c) $O_2^- > O_2 < O_2^+$ (d) $O_2^- < O_2 > O_2^+$

Thinking Process

To calculate bond order, write the molecular orbital configuration of particular species and afterwards using the formula.

Bond order $= \frac{1}{2}$ *[Number of bonding electrons* (N_b)*– Number of anti-bonding electrons* (N_a)*]*

Ans. ***(b)*** Electronic configuration of O_2 (16 electrons)

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

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = 2$$

Electronic confiquration of O_2^+ (15 electrons)

$$= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2 ,\pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^0$$

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

Electronic confiquration of O_2^- (17 electrons)

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

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 7) = 1.5$$

Thus, the order of bond order is $O_2^- < O_2 < O_2^+$

Q. 21 The electronic configuration of the outer most shell of the most electronegative elements is

(a) $2s^2 2p^5$ (b) $3s^2 3p^5$

(c) $4s^2 4p^5$ (d) $5s^2 5p^5$

Ans. ***(a)*** *The electronic configuration represents*

$2s^2 2p^5$ = fluorine = most electronegative element
$3s^2 3p^5$ = chlorine
$4s^2 4p^5$ = bromine
$5s^2 5p^5$ = iodine

Q. 22 Amongst the following elements whose electronic configuration are given below, the one having the highest ionisation enthaply is

(a) $[Ne]3s^2 3p^1$ (b) $[Ne]3s^2 3p^3$

(c) $[Ne]3s^2 3p^2$ (d) $[Ar]3d^{10} 4s^2 4p^3$

Ans. ***(b)*** The electronic configuration of options (b) and (d) have exactly half-filled 3*p* orbitals (b) represents phosphorus and (c) represents arsenic but (b) is smaller in size than (d).

Hence, (b) has highest ionisation enthalpy. Ionisation enthalpy increases left to right in the periodic table as the size decreases.

Multiple Choice Questions (More Than One Options)

Q. 23 Which of the following have identical bond order?

(a) CN^- (b) NO^+ (c) O_2^- (d) O_2^{2-}

Ans. ***(a, b)***

CN^- (number of electrons = 6 + 7 + 1 = 14)
NO^+ (number of electrons = 7 + 8 − 1 = 14)
O_2^- (number of electrons = 8 + 8 + 1 = 17)
O_2^{2-} (number of electrons = 8 + 8 + 2 = 18)

Thus, CN^- and NO^+ because of the presence of same number of electrons, have same bond order.

Q. 24 Which of the following attain the linear structure?

(a) $BeCl_2$ (b) NCO^+ (c) NO_2 (d) CS_2

Ans. *(a, d)*

$BeCl_2$ (Cl — Be — Cl) and CS_2 (S = C = S) both are linear. NCO^+ is non-linear. However, [remember that ^-NCO ($^-N=C=O$) is linear because it is isoelectronic with CO_2]. NO_2 is angular with bond angle 132° and each O — N bond length of 1.20 Å (intermediate between single and double bond).

Q. 25 CO is isoelectronic with

(a) NO^+ (b) N_2 (c) $SnCl_2$ (d) NO_2^-

Thinking Process

Isoelectronic species are those species have same number of electrons but different nuclear charge.

Ans. *(a, b)*

Electrons present in CO = 6 + 8 = 14

Then, In $NO^+ = 7 + 8 - 1 = 14$
In $N_2 = 7 + 7 = 14$
In $SnCl_2$ = (very high) $50 + 17 \times 2 = 50 + 34 = 84$.
In $NO_2^- = 7 + 16 + 1 = 24$

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

(a) CO_2 (b) CCl_4 (c) O_3 (d) NO_2^-

Ans. *(c, d)*

The shape of following species are

CO_2 = linear
CCl_4 = tetrahedral
O_3 = bent
NO_2^- = bent

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

(a) The hybridisation of central atom is sp^3

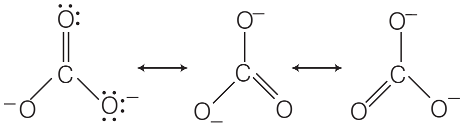
(b) Its resonance structure has one C—O single bond and two C=O double bonds

(c) The average formal charge on each oxygen atom is 0.67 units

(d) All C—O bond lengths are equal

Ans. *(c, d)*

The hybridisation of central atom in CO_3^{2-} is sp^2. Hence, (a) is wrong.



Due to resonance all C—O bond lengths are equal.

$$\text{Formal charge on each O-atom} = \frac{\text{total charge}}{\text{Number of O-atoms}} = \frac{-2}{3} = -0.67 \text{ units.}$$

All C—O bond lengths are equal as mentioned above.

Q. 28 Diamagnetic species are those which contain no unpaired electrons. Which among the following are diamagnetic?

(a) N_2 (b) N_2^{2-}
(c) O_2 (d) O_2^{2-}

Ans. *(a, d)*

(a) Electronic configuration of $N_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$.

It has no unpaired electron indicates diamagnetic species.

(b) Electronic configuration of N_2^{2-} ion $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi p_y^2, \sigma 2p_z^2,$

$$\pi^* 2p_x^1 \approx \pi^* 2p_y^1$$

It has two unpaired electrons, paramagnetic in nature.

(c) Electronic configuration of $O_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2,$

$$\pi^* 2p_x^1 \approx \pi^* 2p_y^1$$

The presence of two unpaired electrons shows its paramagnetic nature.

(d) Electronic configuration of O_2^{2-} ion $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2,$

$$\pi^* 2p_x^2 \approx \pi^* 2p_y^2$$

It contains no unpaired electron, therefore, it is diamagnetic in nature.

Q. 29 Species having same bond order are

(a) N_2 (b) N_2^- (c) F_2^+ (d) O_2^-

Ans. *(c, d)*

Bond order of the following species are calculated using molecular orbital electronic configuration and found as

$N_2 = 3,$
$N_2^- = 2.5$
$F_2^+ = 1.5,$
$O_2^- = 1.5$

Q. 30 Which of the following statements are not correct?

(a) NaCl being an ionic compound is a good conductor of electricity in the solid state
(b) In canonical structure there is a difference in the arrangement of atoms
(c) Hybrid orbitals form stronger bonds than pure orbitals
(d) VSEPR theory can explain the square planar geometry of XeF_4

Ans. *(a, b)*

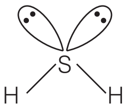
(a) NaCl is a bad conductor of electricity in solid due to the absence of free ions.

(b) Canonical structures differ in the arrangement of electrons, not in the arrangement of atoms.

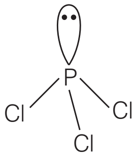
Short Answer Type Questions

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

Ans. Central atom of H_2 is S. There are 6 electrons in its valence shell ($_{16}S = 2, 8, 6$). Two electrons are shared with two H-atoms and the remaining four electrons are present as two lone pairs.



Hence, total pairs of electrons are four (2 bond pairs and 2 lone pairs). Due to the presence of 2 lone pairs the shape becomes distorted tetrahedral or angular or bent (non-linear).



PCl_3–Central atom is phosphorus. There are 5 electrons in its valence shell ($_{15}P = 2, 8, 5$). Three electrons are shared with three Cl-atoms and the remaining two electrons are present as one lone pair.

Hence, total pairs of electrons are four (1 lone pair and 3 bond pairs). Due to the presence of one lone pair, the shape becomes pyramidal (non-planar).

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

Ans. According to molecular orbital theory electronic configurations of O_2^+ and O_2^- species are as follows

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

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

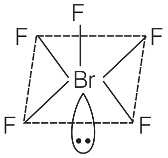
$O_2^- : (\sigma 1s)^2(\sigma^* 1s^2)(\sigma 2s^2)(\sigma^* 2s^2)(\sigma 2p_z)^2(\pi 2p_x^2, \pi 2p_y^2)(\pi^* 2p_x^2, \pi^* 2p_y^1)$

Bond order of $O_2^- = \frac{10-7}{2} = \frac{3}{2} = 1.5$

Higher bond order of O_2^+ shows that it is more stable than O_2^-. Both the species have unpaired electrons. So, both are paramagnetic in nature.

Q. 33 Explain the shape of BrF_5.

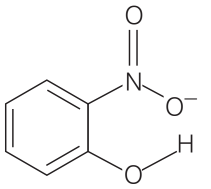
Ans. The central atom Br has seven electrons in the valence shell. Five of these will form bonds with five fluorine atoms and the remaining two electrons are present as one lone pair.



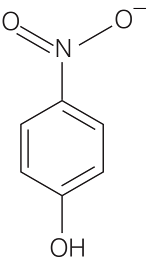
Hence, total pairs of electrons are six (5 bond pairs and 1 lone pair). To minimize repulsion between lone pairs and bond pairs, the shape becomes square pyramidal.

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

(I)



(II)



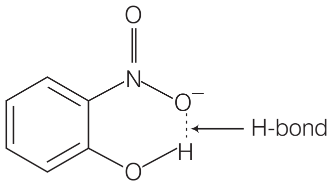
(a) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding?

(b) The melting point of 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 easily and be more soluble in it?

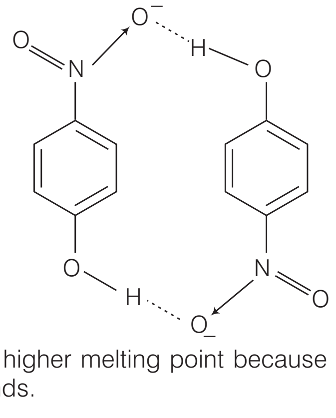
Ans. (a) Compound (I) will form intramolecular H-bonding. Intramolecular H-bonding is formed when H-atom, in between the two highly electronegative atoms, is present within the same molecule. In *ortho*-nitrophenol (compound I), H-atom is in between the two oxygen atoms.

(I)



Compound (II) forms intermolecular H-bonding. In *para*-nitrophenol (II) there is a gap between NO_2 and OH group. So, H-bond exists between H-atom of one molecule and O-atom of another molecule as depicted below.

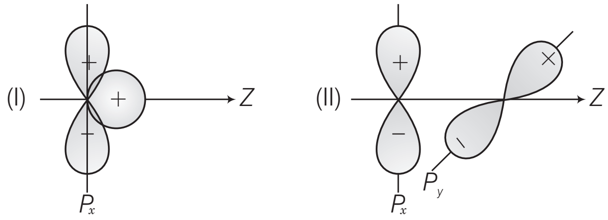
(II)



(b) Compound (II) will have higher melting point because large number of molecules are joined together by H-bonds.

(c) Due to intramolecular H-bonding, compound (I) is not able to form H-bond with water, so it is less soluble in water. While molecules of compound II form H-bonding with H_2O easily, so it is soluble in water.

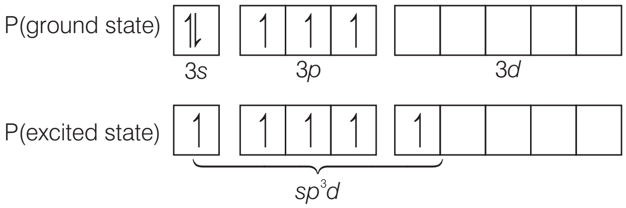
Q. 35 Why does type of overlap given in the following figure not result in bond formation?

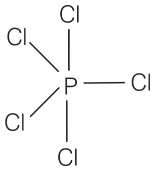


Ans. In the figure (I), area of ++ overlap is equal to +− overlap, so net overlap is zero, while in figure (II), there is no overlap due to different symmetry.

Q. 36 Explain why PCl_5 is trigonal bipyramidal whereas IF_5 is square pyramidal.

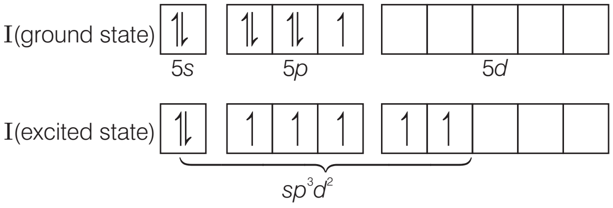
Ans. **PCl_5**–The ground state and the excited state outer electronic configurations of phosphorus ($Z = 15$) are represented below

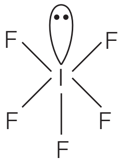




In PCl_5, P is sp^3d hybridised, therefore, its shape is trigonal bipyramidal.

IF_5–The ground state and the excited state outer electronic configurations of iodine ($Z = 53$) are represented below.

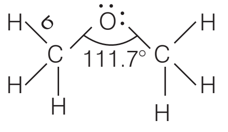




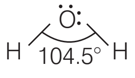
In IF_5, I is sp^3d^2 hybridised, therefore, shape of IF_5 is square pyramidal.

Q. 37 **In both water and dimethyl ether ($CH_3-\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}-CH_3$), 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 has greater bond angle than that of water, however in both the molecules central atom oxygen is sp^3 hybridised with two lone pairs. In dimethyl ether, bond angle is greater (111.7°) due to the greater repulsive interaction between the two bulky alkyl (methyl) groups than that between two H-atoms.



Dimethyl ether



Water

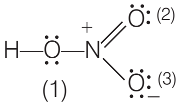
Actually C of CH_3 group is attached to three H-atoms through σ-bonds. These three C—H bond pair of electrons increases the electronic charge density on carbon atom.

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

$$HNO_3, NO_2, H_2SO_4$$

Ans. *The Lewis structure of the following compounds and formal charge on each atom are as*

(i) **HNO_3**



Formal charge on an atom in a Lewis structure

$$= [\text{total number of valence electrons in free atom}]$$
$$- [\text{total number of non-bonding (lone pairs) electrons}]$$
$$- \frac{1}{2} [\text{total number of bonding or shared electrons}]$$

$$\text{Formal charge on H} = 1 - 0 - \frac{1}{2} \times 2 = 0$$

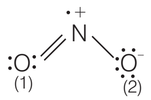
$$\text{Formal charge on N} = 5 - 0 - \frac{1}{2} \times 8 = 1$$

$$\text{Formal charge on O(1)} = 6 - 4 - \frac{1}{2} \times 4 = 0$$

$$\text{Formal charge on O(2)} = 6 - 4 - \frac{1}{2} \times 4 = 0$$

$$\text{Formal charge on O(3)} = 6 - 6 - \frac{1}{2} \times 2 = -1$$

(ii) **NO_2**

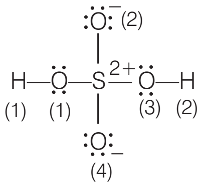


$$\text{Formal charge on O(1)} = 6 - 4 - \frac{1}{2} \times 4 = 0$$

$$\text{Formal charge on N} = 5 - 1 - \frac{1}{2} \times 6 = +1$$

$$\text{Formal charge on O(2)} = 6 - 6 - \frac{1}{2} \times 2 = -1$$

(iii) **H_2SO_4**



$$\begin{array}{ccccccc} & & & :\ddot{O}:^{-}\,(2) & & & \\ & & & | & & & \\ H & - & \underset{\cdot\cdot}{\ddot{O}} & -\,S^{2+}\,- & \underset{\cdot\cdot}{\ddot{O}} & - & H \\ (1) & & (1) & | & (3) & & (2) \\ & & & :\underset{\cdot\cdot}{O}:^{-} & & & \\ & & & (4) & & & \end{array}$$

Formal charge on H(1) or H(2) $= 1 - 0 - \frac{1}{2} \times 2 = 0$

Formal charge on O(1) or O(3) $= 6 - 4 - \frac{1}{2} \times 4 = 0$

Formal charge on O (2) or O (4) $= 6 - 6 - \frac{1}{2} \times 2 = -1$

Formal charge on S $= 6 - 0 - \frac{1}{2} \times 8 = +2$

Q. 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.**

$$N_2, N_2^+, N_2^-, N_2^{2+}$$

Ans. Electronic configuration of N-atom ($Z = 7$) is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. Total number of electrons present in N_2 molecule is 14, 7 from each N-atom. From the view of various rules for filling of molecular orbitals, the electronic configuration of N_2 molecule will be

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

Comparative study of the relative stability and the magnetic behaviour of the following species

(i) **N_2 molecule** $\sigma 1s^2, \sigma^* s^2, \sigma 2s^2, \sigma^* 2s^2, \pi p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

Here, $N_b = 10$, $N_a = 4$.

Hence, Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = 3$

Hence, presence of no unpaired electron indicates it to be diamagnetic.

(ii) **N_2^+ ions** $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^1$

Here, $N_b = 9$, $N_a = 4$ so that BO $= \frac{1}{2}(9 - 4) = \frac{5}{2} = 2.5$

Further, as N_2^+ ion has one unpaired electron in the $\sigma(2p_2)$ orbital, therefore, it is paramagnetic in nature.

(iii) **N_2^- ions** $\sigma 1s^2, \sigma^* s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x^1$

Here, $N_b = 10$, $N_a = 5$ so that BO $= \frac{1}{2}(10 - 5) = \frac{5}{2} = 2.5$

Again, as it has one unpaired electron in the $\pi^*(2p_x)$ orbital, therefore, it is paramagnetic.

(iv) **N_2^{2+} ions** $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$

Here, $N_b = 8$, $N_a = 4$. Hence, BO $= \frac{1}{2}(8 - 4) = 2$

Presence of no unpaired electron indicates it to be diamagnetic in nature.

As bond dissociation energies are directly proportional to the bond orders, therefore, the dissociation energies of these molecular species in the order.

$$N_2 > N_2^- = N_2^+ > N_2^{2+}$$

As greater the bond dissociation energy, greater is the stability, the stability of these species is also in the above order.

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

(a) $N_2 \longrightarrow N_2^+ + e^-$ (b) $O_2 \longrightarrow O_2^+ + e^-$

Ans. According to molecular orbital theory, electronic configurations and bond order of N_2, N_2^+, O_2 and O_2^+ species are as follows

$$N_2\ (14e^-) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \ (\pi\, 2p_x^2 \approx \pi 2p_y^2), \sigma 2p_z^2$$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10-4) = 3$$

$$N_2^+\ (13e^-) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \ (\pi\, 2p_x^2 \approx \pi 2p_y^2)\ \sigma 2p_z^1$$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(9-4) = 2.5$$

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

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10-6) = 2$$

$$O_2^+\ (15e^-) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, (\pi 2p_x^2 \approx \pi 2p_y^2), \ (\overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y)$$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10-5) = 2.5$$

(a) $\underset{\text{B.O.} = 3}{N_2} \longrightarrow \underset{\text{B.O.} = 2.5}{N_2^+} + e^-$

Thus, bond order decreases.

(b) $\underset{\text{B.O} = 2}{O_2} \longrightarrow \underset{\text{B.O} = 2.5}{O_2^+} + e^-$

Thus, bond order increases.

Q. 41 Give reason for the following.

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

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

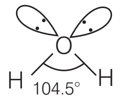
(c) Ethyne molecule is linear.

Ans. (a) A covalent bond is formed by the overlap of atomic orbitals. The direction of overlapping gives the direction of bond. In ionic bond, the electrostatic field of an ion is non-directional.

Each positive ion is surrounded by a number of anions in any direction depending upon its size and *vice-versa.* That's why covalent bonds are directional bonds while ionic bonds are non-directional.

(b) In H_2O, oxygen atom is sp^3 hybridised with two lone pairs. The four sp^3 hybridised orbitals acquire a tetrahedral geometry with two corners 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 the molecule thus acquires a V-shape or bent structure (angular structure).



In CO_2 molecule, carbon atom is sp-hybridised. The two sp hybrid orbitals are oriented in opposite direction forming an angle of 180°.

$$O \overset{\pi}{\underset{\sigma}{=}} C \overset{\pi}{\underset{\sigma}{=}} O$$

That's why H_2O molecule has bent structure whereas CO_2 molecule is linear.

(c) In ethyne molecule, both the carbon atoms are sp hybridised, having two unhybridised orbitals, *i.e.,* $2p_x$ and $2p_y$. The two sp hybrid orbitals of both the carbon atoms are oriented in opposite direction forming an angle of 180°.

$$H—C \overset{\sigma}{\equiv} C—H$$
$$2\pi\text{-bond}$$

That's why ethyne molecule is linear.

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

Ans. **Ionic bond** The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as the electrovalent bond or ionic bond. *e.g.,* the formation of NaCl from sodium and chlorine can be explained as

$$\underset{[Ne]3s^1}{Na} \longrightarrow \underset{[Ne]}{Na^+} + e^-$$

$$\underset{[Ne]3s^2 3p^5}{Cl} + e \longrightarrow \underset{[Ne]3s^2 3p^6 \text{ or } [Ar]}{Cl^-}$$

$$Na^+ + Cl^- \longrightarrow NaCl \text{ or } Na^+Cl^-$$

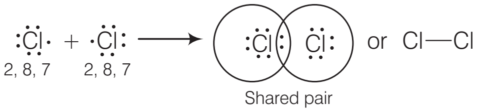
Similarly, the formation of CaF_2 may be shown as

$$\underset{[Ar]4s^2}{Ca} \longrightarrow \underset{[Ar]}{Ca^{2+}} + 2e^-$$

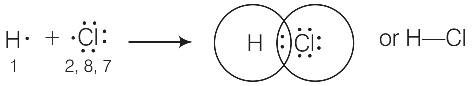
$$\underset{[He]\ 2s^2 2p^5}{F} + e^- \longrightarrow \underset{[He]\ 2s^2 2p^6 \text{ or } [Ne]}{F^-}$$

$$Ca^{2+} + 2F^- \longrightarrow CaF_2 \text{ or } Ca^{2+}(F^-)_2$$

Covalent bond The bond formed between the two atoms by mutual sharing of electrons between them is called covalent bond. *e.g.,* the formation of chlorine molecule can be explained as



Similarly, in the formation of HCl



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

N—H, F—H, C—H and O—H

Ans. Greater is the electronegativity difference between the two bonded atoms, greater is the ionic character.

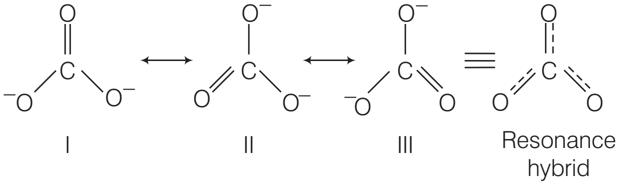
Bond	N—H	F—H	C—H	O—H
Electronegativity difference	(3.0 – 2.1) = 0.9	(4.0 – 2.1) = 1.9	(2.5 – 2.1) = 0.4	(3.5 – 2.1) = 1.4

Therefore, increasing order of ionic character of the given bonds is as follows

C—H < N—H < O—H < F—H

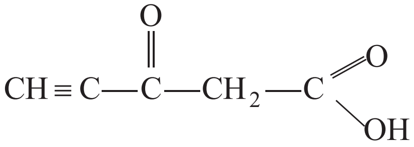
Q. 44 Explain why CO_3^{2-} ion cannot be represented by a single Lewis structure. How can it be best represented?

Ans. A single Lewis structure of CO_3^{2-} ion cannot explain all the properties of this ion. *It can be represented as a resonance hybrid of the following structures*

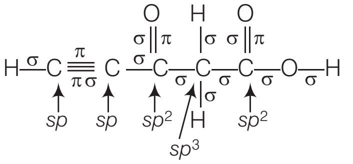


If, it were represented only by one structure, there should be two types of bonds, *i.e.*, C ═O double bond and C— O single bonds but actually all bonds are found to be identical with same bond length and same bond strength.

Q. 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. *The hybridisation and type of bonds of each carbon in the molecule given below*



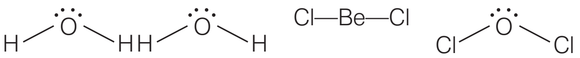
σ-bonds = 11

π-bonds = 4

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

H_2O, HOCl, $BeCl_2$, Cl_2O

Ans. *The structure of the given molecules are*



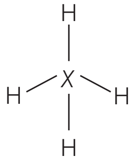
Therefore, only $BeCl_2$ is linear and rest of the molecules are non-linear.

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

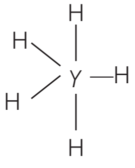
(a) Write the molecular formula of the compounds formed by these elements individually with hydrogen.

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

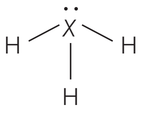
Ans. **(a)**



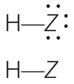
.XH_4



XY_5



.XH_3



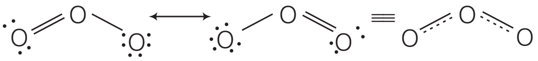
(b) *Z* has seven electrons in its valence shell. It is the most electronegative element. Therefore, H*Z* will have the highest dipole moment.

Q. 48 Draw the resonating structure of

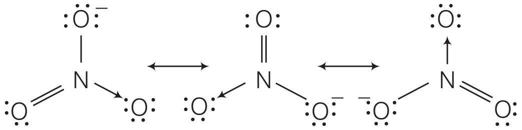
(a) ozone molecule

(b) nitrate ion

Ans. **(a)** The resonating structure of ozone molecule may be written as



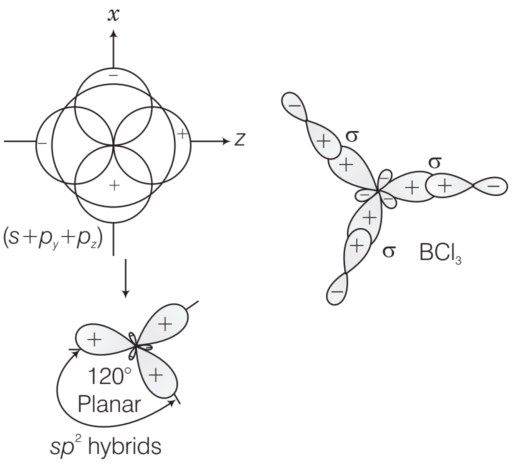
(b) The resonating structure of nitrate ion (NO_3^-) is



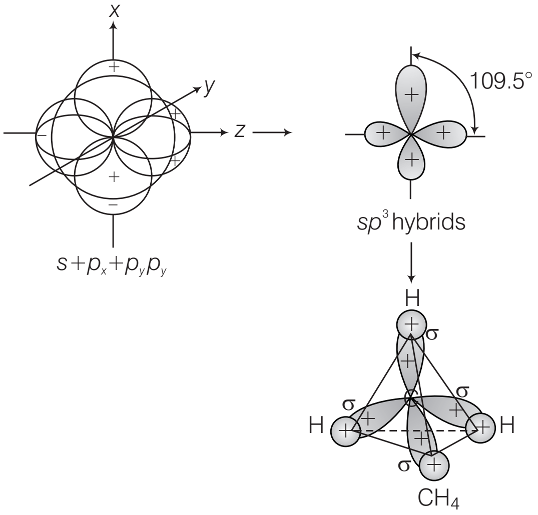
Q. 49 Predict the shapes of the following molecules on the basis of hybridisation.

$$BCl_3, CH_4, CO_2, NH_3$$

Ans. In BCl_3, the geometry is trigonal planar is due to sp^2 hybridisation.



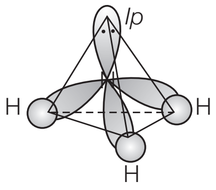
The shape of CH_4 is tetrahedral due to sp^3 hybridisation.



CO_2 show linear shape because of sp hybridisation.

$$:\ddot{O}=C=\ddot{O}:$$

The geometry of NH_3 is pyramidal shape and has sp^3 hybridisation.



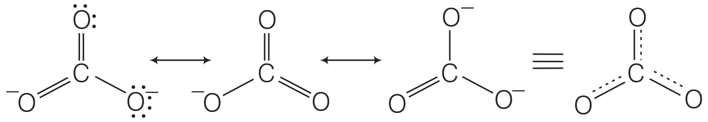
Ammonia, NH_3

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

Thinking Process

To explain the reason of equal in length of C—O bonds, it should keep in mind about the resonance. As a result of resonance, the bond length in a molecule become equal.

Ans. Carbonate ion (CO_3^{2-}) = 3 bond pair + 1 lone pair ⇒ trigonal planar



Due to resonance all C—O bond length are equal.

Q. 51 What is meant by the term average bond enthalpy? Why is there difference in bond enthalpy of O—H bond in ethanol (C_2H_5OH) and water?

Ans. All the similar bonds in a molecule do not have the same bond enthalpies. *e.g.,* in H_2O(H — O — H) molecule after the breaking of first O—H bond, the second O—H bond undergoes some change because of changed chemical environment.

Therefore, in polyatomic molecules the term mean or average bond enthalpy is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken.

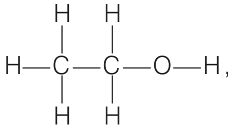
e.g., $H_2O(g) \longrightarrow H(g) + OH(g)$;

$\Delta_a H_1^\circ = 502 \text{ kJ mol}^{-1}$ $OH(g) \longrightarrow H + O(g)$;

$$\Delta_a H_2^\circ = 427 \text{ kJ mol}^{-1}$$

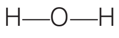
$$\text{Average O—H bond enthalpy} = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

The bond enthalpies of O—H bond in C_2H_5OH and H_2O are different because of the different chemical (electronic) environment around oxygen atom.



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$$

(C_2H_5OH)



$$\mathrm{H{-}O{-}H}$$

(H_2O)

Matching The Columns

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

Column I	Column II
A. SF_4	1. sp^3d^2
B. IF_5	2. d^2sp^3
C. NO_2^+	3. sp^3d
D. NH_4^+	4. sp^3
	5. sp

Ans. **A.** → (3) **B.** → (1) **C.** → (5) **D.** → (4)

A. SF_4 = number of *bp* (4) + number of *lp* (1)

= sp^3d hybridisation

B. IF_5 = number of *bp* (5) + number of *lp* (1)

= sp^3d^2 hybridisation

C. NO_2^+ = number of *bp* (2) + number of *lp* (0)

= *sp* hybridisation

D. NH_4^+ = number of *bp* (4) + number of *lp* (0)

= sp^3 hybridisation.

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

Column I	Column II
A. H_3O^+	1. Linear
B. $HC \equiv CH$	2. Angular
C. ClO_2^-	3. Tetrahedral
D. NH_4^+	4. Trigonal bipyramidal
	5. Pyramidal

Ans. **A.** → (5) **B.** → (1) **C.** → (2) **D** → (3)

A. $H_3O^+ = 3bp + 1lp$ pyramidal shape

B. $HC \equiv CH \Rightarrow$ linear as *sp* hybridised shape

C. $ClO_2^- = 2bp + 2lp \Rightarrow$ angular shape

D. $NH_4^+ = 4bp + 0lp \Rightarrow$ tetrahedral shape

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

Column I		Column II	
A.	NO	1.	1.5
B.	CO	2.	2.0
C.	O_2^-	3.	2.5
D.	O_2	4.	3.0

Ans. **A.** → (3) **B.** → (4) **C.** → (1) **D.** → (2)

A. NO $(7 + 8 = 15) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1$

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

B. CO $(6 + 8 = 14) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \simeq \pi 2p_y^2$

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

C. O_2^- $(8 + 8 + 1 = 17) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^2 \simeq \pi^* 2p_y^1$

$$\text{Bond order} = \frac{10-7}{2} = 1.5$$

D. $O_2 (8 + 8 = 16) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1 \simeq \pi^* 2p_y^1$

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

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

Column I		Column II	
A.	Hydrogen bond	1.	C
B.	Resonance	2.	LiF
C.	Ionic solid	3.	H_2
D.	Covalent solid	4.	HF
		5.	O_3

Ans. **A.** → (4) **B.** → (5) **C.** → (2) **D.** → (1)

A. Hydrogen bond → HF

B. Resonance → O_3

C. Ionic bond → LiF

D. Covalent solid → C

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

Column I	Column II
A. Tetrahedral	1. sp^2
B. Trigonal	2. sp
C. Linear	3. sp^3

Ans. **A.** → (3) **B.** → (1) **C.** → (2)

A. Tetrahedral shape – sp^3 hybridisation

B. Trigonal shape – sp^2 hybridisation

C. Linear shape – sp hybridisation

Assertion and Reason

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 in each question.*

Q. 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.

(a) A and R both are correct and R is the correct explanation of A
(b) A and R both are correct, but R is not the correct explanation of A
(c) A is true, but R is false
(d) A and R both are false

Ans. ***(a)*** Assertion and reason both are correct and reason is the correct explanation of assertion.

$$\underset{(2,\ 8,\ 1)}{\text{Na}} + \underset{(2,\ 8,\ 7)}{\text{Cl}} \longrightarrow \underset{\substack{(2,\ 8)\\(2,\ 8,\ 8)}}{\text{NaCl}}$$

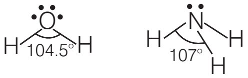
Here both Na^+ and Cl^- have complete octet hence NaCl is stable.

Q. 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.

(a) A and R both are correct and R is the correct explanation of A
(b) A and R both are correct but R is not the correct explanation of A
(c) A is true, but R is false
(d) A and R both are false

Ans. ***(a)*** Assertion and reason both are correct and reason is the correct explanation of assertion.



sp^3–hybridised sp^3–hybridised

Q. 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.

(a) A and R both are correct and R is the correct explanation of A

(b) A and R both are correct, but R is not the correct explanation of A

(c) A is true, but R is false

(d) A and R both are false

Ans. *(d)* **Correct assertion** The bond enthalpies of the two O—H bonds in H—O—H are not equal.

Correct reason This is because electronic environment around O is not same after breakage of one O—H bond.

Long Answer Type Questions

Q. 60 (a) Discuss the significance/applications of dipole moment.

(b) Represent diagrammatically the bond moments and the resultant dipole moment in CO_2 , NF_3 and $CHCl_3$.

Ans. **(a)** *The applications of dipole moment are*

(i) The dipole moment helps to predict whether a molecule is polar or non-polar. As $\mu = q \times d$, greater is the magnitude of dipole moment, higher will be the polarity of the bond. For non-polar molecules, the dipole moment is zero.

(ii) *The percentage of ionic character can be calculated as*

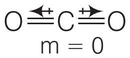
$$\text{Percentage of ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100$$

(iii) Symmetrical molecules have zero dipole moment although they have two or more polar bonds (in determination of symmetry).

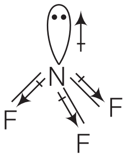
(iv) It helps to distinguish between *cis* and *trans* isomers. Usually *cis*-isomer has higher dipole moment than *trans* isomer.

(v) It helps to distinguish between *ortho*, *meta* and *para* isomers. Dipole moment of *para* isomer is zero. Dipole moment of ortho isomer is greater than that of *meta* isomer.

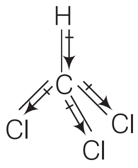
(b)



m = 0



m = 0.24 D

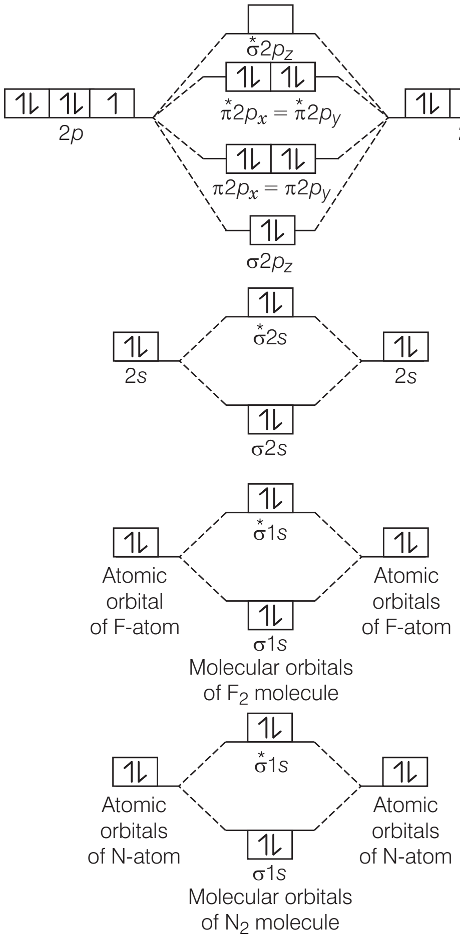


m = 1.03 D

Q. 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 of N- atom ${}_7N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

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

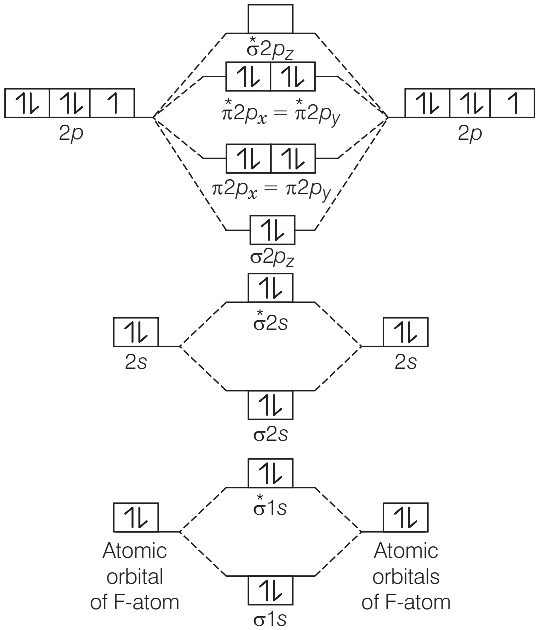


Bond order $= \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10 - 4) = 3.$

Bond order value of 3 means that N_2 contains a triple bond.

Formation of F$_2$ molecule, $_9\text{F} = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$

F$_2$ molecule = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z{}^2, \pi 2p_x{}^2 \approx \pi 2p_y{}^2, \pi^* 2p^2{}_x \approx \pi^* 2p^2{}_y$



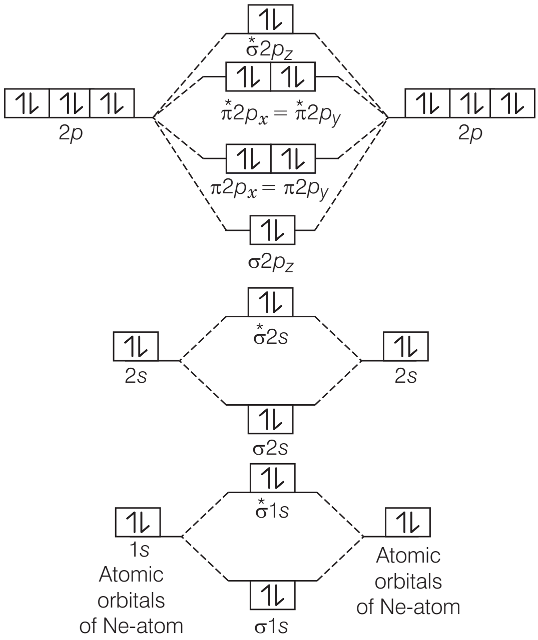
Molecular orbitals of F$_2$ molecule

Bond order = $\frac{1}{2}[N_b - N_a] = \frac{1}{2}(10 - 8) = 1$

Bond order value 1 means that F$_2$ contains single bond.

Formation of Ne$_2$ molecule $_{10}\text{Ne} = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$

Ne$_2$molecule = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z{}^2, \pi 2p_x{}^2 \approx \pi 2p_y{}^2, \pi^* 2p^2{}_x$
$\approx \pi^* 2p^2{}_y, \sigma^* 2p_z{}^2$



Molecular orbitals of Ne$_2$ molecule

Bond order $= \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10 - 10) = 0$

Bond order value zero means that there is no formation of bond between two Ne-atoms. Hence, Ne_2 molecule does not exist.

Q. 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 (VBT) was introduced by Heitler and London (1927) and developed further by Pauling and other. VBT is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridisation of atomic orbitals and the principles of variation and superposition.

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

i.e., $N_A - e_A$ 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

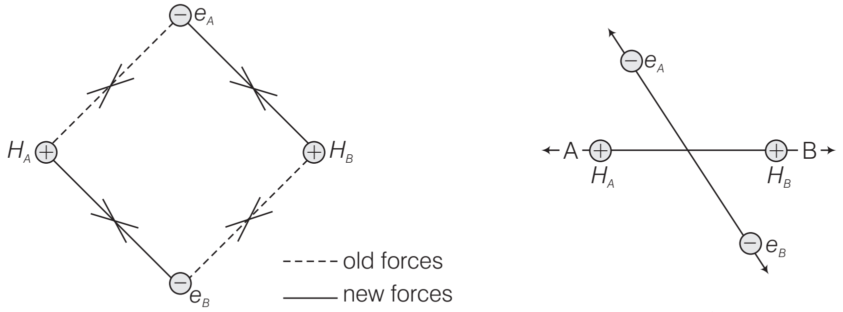
(i) electrons of two atoms like $e_A - e_B$

(ii) nuclei of two atoms like $N_A - N_B$

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

Experimentally, we have 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.

Hence, a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage, two H-atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.



Attractive forces

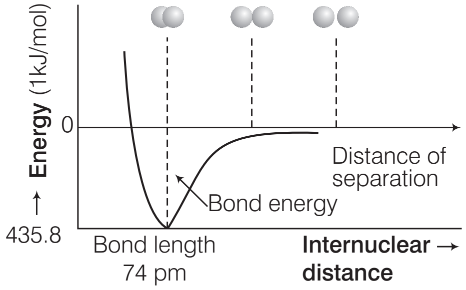
Repulsive forces

H_2

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 the given figure. Conversely 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

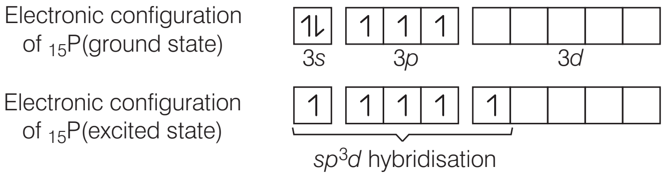
$$H_2(g) + 435.8\text{kJ mol}^{-1} \longrightarrow H(g) + H(g)$$



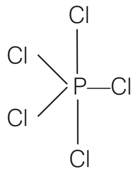
The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H-atoms. The minimum in the curve corresponds to the most stable state or H_2.

Q. 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**



In PCl_5, phosphorus is sp^3d hybridised to produce a set of five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal. These five sp^3d hybrid orbitals overlap with singly occupied p-orbitals of Cl-atoms to form five P—Cl sigma bonds.

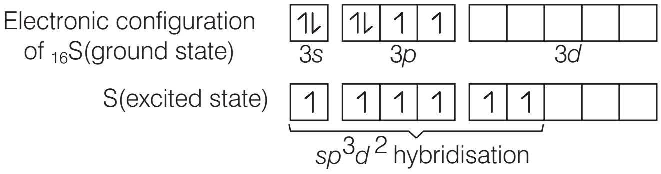


(Trigonal bipyramidal)
PCl_5

Three P—Cl bonds lie in one plane and make an angle of 120° with each other. These bonds are called equatorial bonds. The remaining two P—Cl bonds one lying above and other lying below the plane make an angle of 90° with the equatorial plane.

These bonds are called axial bonds. Axial bonds are slightly longer than equatorial bonds because axial bond pairs suffer more repulsive interaction from the equatorial bond pairs.

Formation of SF_6

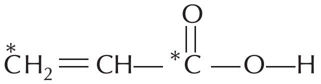


In SF_6, sulphur is sp^3d^2 hybridised to produce a set of six sp^3d^2 hybrid orbitals which are directed towards the six corners of a regular octahedron. These six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S—F sigma bonds.

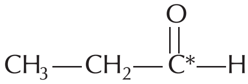
Thus, SF_6 molecule has a regular octahedral geometry and all S—F bonds have same bond length.

Q. 64 (a) Discuss the concept of hybridisation. What are its different types in a carbon atom?

(b) What is the type of hybridisation of carbon atoms marked with star?

(i) 
$\overset{*}{C}H_2{=}CH{-}{}^*\overset{\overset{O}{\|}}{C}{-}O{-}H$

(ii) $CH_3{-}\overset{*}{C}H_2{-}OH$

(iii) 
$CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{}^*{-}H$

(iv) $\overset{*}{C}H_3{-}CH{=}CH{-}CH_3$

(v) $CH_3{-}\overset{*}{C}{\equiv}CH$

Ans. Hybridisation It can be defined as the process of intermixing of the orbitals of slightly different energy or of same energy to produce entirely new orbitals of equivalent energy, identical shapes and symmetrically disposed in plane. New orbitals formed are called hybrid orbitals.

Only the orbitals of an isolated single atom can undergo hybridisation. The hybrid orbitals generated are equal in number to that of the pure atomic orbitals which mix up.

Hybrid orbitals do not make π, pi-bonds. If there are π-bonds, equal number of atomic orbitals must be left unhybridised for π-bonding.

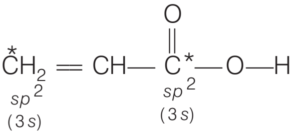
Like atomic orbitals, hybrid orbitals cannot have more than two electrons of opposite spins.

Types of hybridisation in carbon atoms

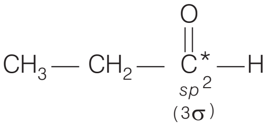
(a) (i) **Diagonal or** sp**-hybridisation** All compounds of carbon containing $C{\equiv}C$ triple bond like ethyne (C_2H_2).

(ii) **Trigonal or** sp^2**-hybridisation** All compounds of carbon containing $C{=}C$ (double bond) like ethene (C_2H_4).

(iii) **Tetrahedral or** sp^3**-hybridisation** All compounds of carbon containing $C{-}C$ single bonds only like ethane (C_2H_6).

(b) (i) 
$\underset{\substack{sp^2\\(3s)}}{\overset{*}{C}H_2}{=}CH{-}\underset{\substack{sp^2\\(3s)}}{\overset{\overset{O}{\|}}{C}{}^*}{-}O{-}H$

(ii) $CH_3\underset{\substack{sp^3\\(4\sigma)}}{\overset{*}{C}H_2}OH$

(iii) 
$CH_3{-}CH_2{-}\underset{\substack{sp^2\\(3\sigma)}}{\overset{\overset{O}{\|}}{C}{}^*}{-}H$

(iv) $\underset{\substack{sp^3\\(4\sigma)}}{\overset{*}{C}H_3}{-}CH{=}CH{-}CH_3$

(v) $CH_3{-}\underset{\substack{sp\\(2\sigma)}}{\overset{*}{C}}{\equiv}CH$

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

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

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

For oxygen and fluorine order of energy of molecular orbitals is given below

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

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.

Q. 65 Which of the following statements is correct?

(a) In the formation of dioxygen from oxygen atoms 10 molecular orbitals will be formed

(b) All the molecular orbitals in the dioxygen will be completely filled

(c) Total number of bonding molecular orbitals will not be same as total number of anti-bonding orbitals in dioxygen

(d) Number of filled bonding orbitals will be same as number of filled anti-bonding orbitals

Ans. ***(a)*** In the formation of dioxygen from oxygen atoms, ten molecular orbitals will be formed.

$$O_2 = \underset{1}{\underline{\sigma 1s^2}}\ \underset{2}{\underline{\sigma^* 1s^2}}\ \underset{3}{\underline{\sigma 2s^2}}\ \underset{4}{\underline{\sigma^* 2s^2}}\ \underset{5}{\underline{\sigma_2 p_z^2}}\ \underset{6}{\underline{\pi 2p_x^2}}\ \underset{7}{\underline{\pi 2p_y^2}}\ \underset{8}{\underline{\pi^* 2p_x^1}}\ \underset{9}{\underline{\pi^* 2p_y^1}}\ \underset{10}{\underline{\sigma^* 2p_z^0}}$$

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

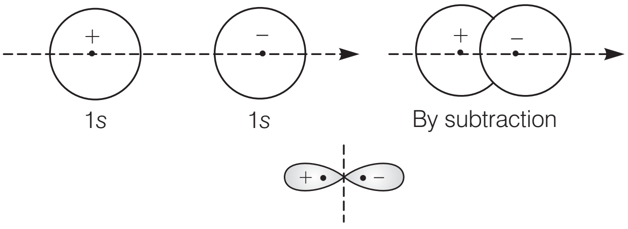
(a) $\sigma^* 1s$

(b) $\sigma^* 2p_z$

(c) $\pi 2p_x$

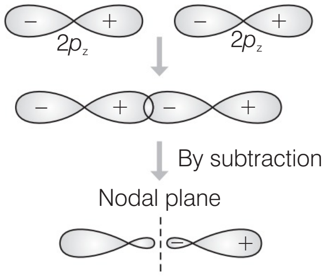
(d) $\pi^* 2p_y$

Ans. ***(d)*** Nodal plane are $\sigma^* 1s = 1$, $\sigma^* 2p_z = 1$, $\pi 2p_x = 1$, $\pi^* 2p_y = 2$

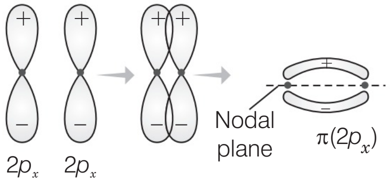


σ* (1s)
Anti-bonding molecular orbital

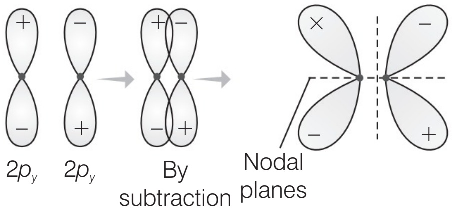
The molecular orbitals whose number of nodal planes are as



σ* (2p_z)



π(2p_x)



π* (2p_y)

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

(a) O_2, N_2 (b) O_2^+, N_2^-

(c) O_2^-, N_2^+ (d) O_2^-, N_2^-

Ans. *(b)* On the basec of molecular orbetal therory we can calculate bond order of molecules ions as

$$BO = \frac{1}{2}(N_b - N_a)$$

Molecular orbital electronic configuration (MOEC) of N_2 is

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

Bond order of $N_2 = \frac{1}{2}(10 - 4) = 3$

MOEC of $N_2{}^+ = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \simeq \pi 2p_y^2, \sigma 2p_2$

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

MOEC of $N_2{}^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \simeq \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x^1 \simeq \pi^* 2p_y$

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

MOEC of $O_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \simeq \pi 2p_y{}^2, \pi^* 2p_x^1 \simeq \pi^* 2p_y^1$

BO of $O_2 = \frac{1}{2}(10 - 6) = 2$

MOEC of $O_2^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \simeq \pi 2p_y^2, \pi^* 2p_x^2 \simeq \pi^* 2p_y^1$

BO of $O_2^- = \frac{1}{2}(10-7) = 1.5$

MOEC of $O_2^+ = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \simeq \pi 2p_y^2, \pi^* 2p_x^2 \simeq \pi^* 2p_y$

BO of $O_2^+ = \frac{1}{2}(10-5) = 2.5$

(a) Bond order of O_2 and N_2 are 2 and 3, respectively.

(b) Bond order of both O_2^+ and N_2^- are 2.5.

(c) Bond order of O_2^- and N_2^+ are 1.5 and 2.5, respectively.

(d) Bond order of O_2^- and N_2^- are 1.5 and 2.5 respectively.

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

(a) O_2 (b) Ne_2

(c) N_2 (d) F_2

Ans. *(c)* Total number of electrons present in N_2 molecule is 14.

The electronic configuration of N_2 molecule will be

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

Note *The increasing order of energies of various molecular orbitals for* O_2 *and* F_2 *is given below* $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x \approx \pi 2p_y) < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$

However, this sequence of energy levels of MO is not correct for the remaining molecules such as Li_2, Be_2, B_2, C_2 *and* N_2. *For these molecules, the increasing order of energies of various MO is*

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