49. In which pair of species, both species do have the similar geometry ?

(A) CO_2, SO_2 **(B)** NH_3, BH_3

(C) CO_3^{2-}, SO_3^{2-} **(D)** SO_4^{2-}, ClO_4^-

50. In which of the following arrangements, the sequence is not strictly according to the property written against it ?

(A) $NH_3 < PH_3 < As\,H_3 < SbH_3$: increasing basic strength

(B) $B < C < O < N$: increasing first inoization enthalpy

(C) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power

(D) $HF < HCl < HBr < HI$: increasing acid strength

51. Which of the following substances has the highest melting point ?

(A) NaCl **(B)** KCl

(C) MgO **(D)** BaO

52. Which of the following statement is correct ?

(A) $FeCl_2$ is more covalent than $FeCl_3$

(B) $FeCl_3$ is more covalent than $FeCl_2$

(C) Both $FeCl_2$ and $FeCl_3$ are equally covalent

(D) $FeCl_2$ and $FeCl_3$ do not have any covalent character

53. Which one of the following compounds has sp^2-hybridisation ?

(A) CO_2 **(B)** SO_2

(C) N_2O **(D)** CO

Subjective Type :

54. Draw structures of following species.

(a) SbF_4^- **(b)** SF_5^- **(c)** SeF_3^+ **(d)** SOF_4 **(e)** ClO_2F_3 **(f)** XeO_3F_2 **(g)** HCP **(h)** IOF_4^- **(i)** $SeOCl_2$

(j) $XeOF_2$ **(k)** $ClOF_3$ **(l)** $SOCl_2$ **(m)** COF_2 **(n)** SNF_3 **(o)** XeO_3 **(p)** IOF_5 **(q)** IOF_3 **(r)** $XeOF_4$

MOLECULAR ORBITAL THEORY Section - 3

Molecular Orbital Theory for the Formation of Covalent Bond

1. This theory suggest that when two atoms come close towards each other, then the atomic orbitals of each atom overlaps with each other to form new bigger orbitals known as Molecular Orbitals (MO).

2. When atomic orbitals overlap then two MOs are produced.

  (a) Bonding Molecular Orbital (BMO)

  (b) Anti-bonding Molecular Orbital (ABMO)

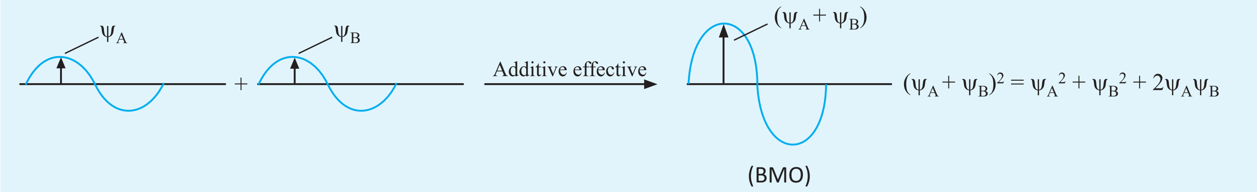
3. Bonding molecular orbital has less energy than separate atomic orbital.

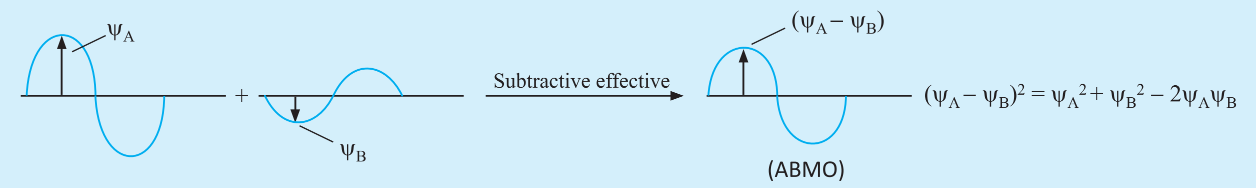
4. Anti-bonding molecular orbital has higher energy than separate atomic orbital.

5. These new MOs are spread over the atomic nuclei of both the atoms, consequently, the electrons present in the MOs are attracted by both the nuclei.

Linear Combination of Atomic Orbitals (LCAO)

According to the principle of Linear Combination of Atomic Orbitals (LCAO), bonding MO is formed by addition of wave functions (constructive interference) of the electron waves of atomic orbitals while anti-bonding MO is formed by substraction of the wave functions of the atomic orbitals (destructive interference).





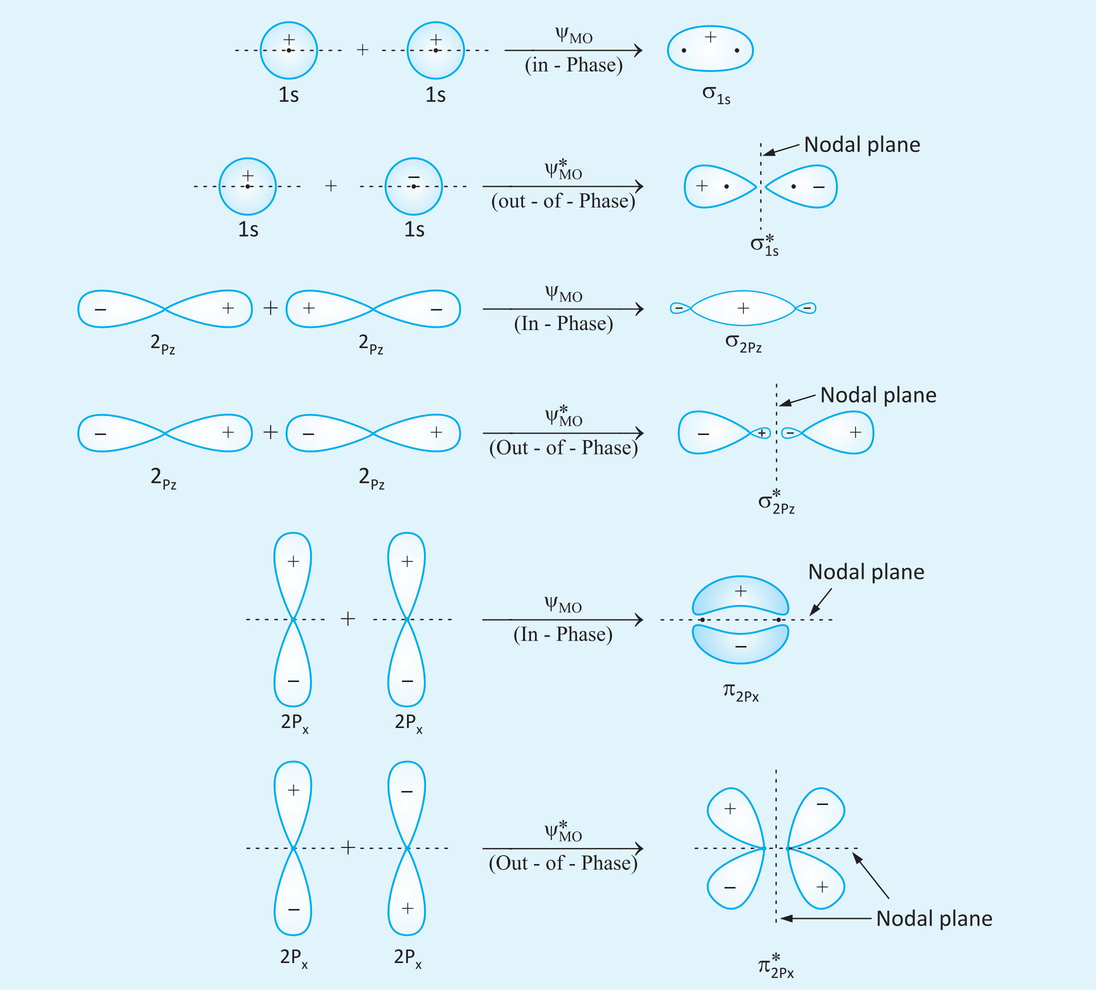
Note : ψ_{MO} is an in-phase (bonding) interaction whereas ψ^*_{MO} is an out of phase (anti-bonding) interaction. Further out of phase interaction results in a nodal plane in the MOs.

1. Only AO's of comparable energies and proper orientations combine to form MO's. For example, 1*s* can combine with 1s and not with 2*s*. Similarly, if *z* is the molecular axis p_z can combine with p_z but not with p_x or p_y to form σ-molecular orbitals.

2. The bonding MO's are represented as σ and π while the corresponding anti-bonding MO's are represented as σ^* and π^*. Of the 2*p* orbitals, if *z* is the molecular axis, two p_z orbitals form σ bond, i.e., $\sigma(2p_z)$ while $2p_x$ and $2p_y$ orbitals form π - bonds, i.e., $\pi(2p_x)$, $\pi(2p_y)$, $\pi^*(2p_x)$ and $\pi^*(2p_y)$.

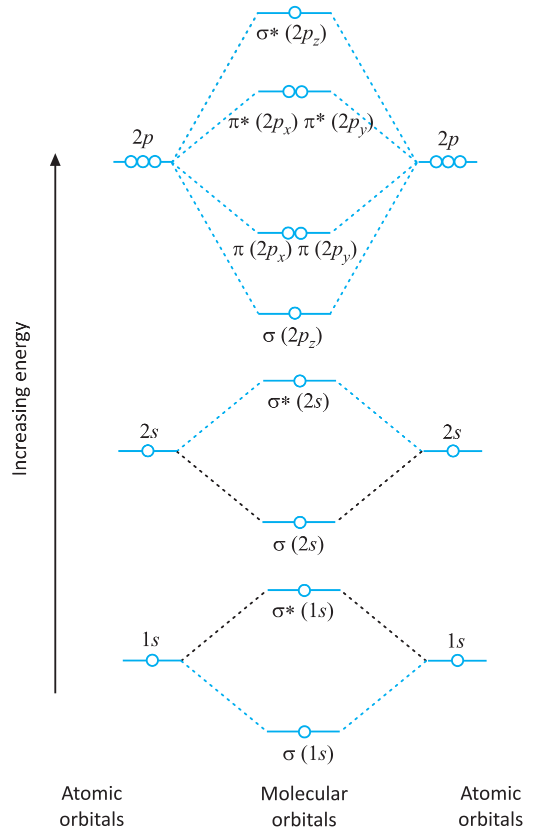
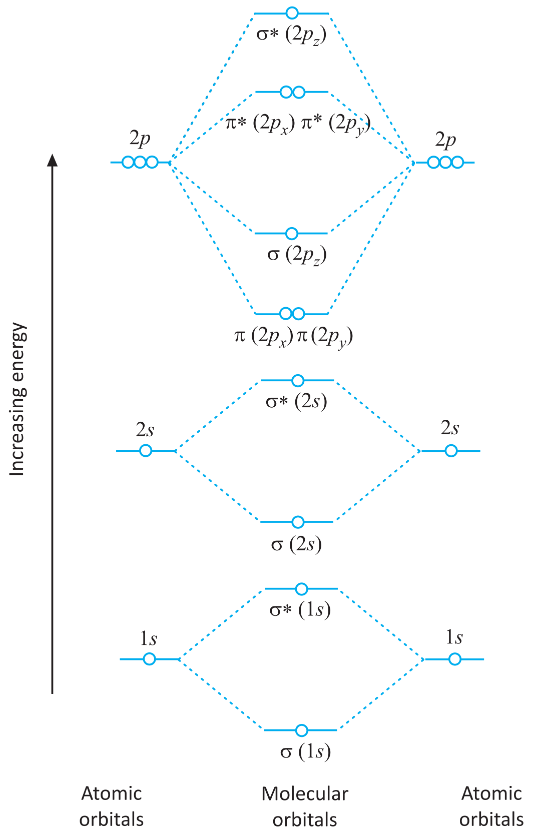
3. The shapes of MO's formed depend upon the type of the combining AO's.

Atomic Orbital Interaction diagrams :



4. The filling of the MO's occurs according to the same principle as applicable to filling of AO's i.e., Aufbau principle (MO's are filled in order of their increasing energies), Pauli's exclusion principle (a MO can have a maximum of two electrons and these must have opposite spins) and Hund's rule of maximum multiplicity (pairing of electrons in degenerate MO's does not take place until each one of the them has one electron with the same spin).

5. Molecular Orbital Diagram :

<table>
<tr><th>For atoms with atomic number greater than 7 e.g., O_2, F_2 or For species with total number of electrons greater than 14 e.g., NO</th><th>For atoms with atomic number less than or equal to 7 e.g., H_2, C_2, N_2 or For species with total number of electrons less than or equal to 14 e.g., B_2 C_2, CN^-</th></tr>
<tr><td>
</td><td>
</td></tr>
</table>

Note : The ordering of the MOs in B_2, C_2 and N_2 is different from that in F_2 and O_2 because of orbital mixing.

6. Magnetic Character :

If all the electrons in a molecule are paired, the compound is diamagnetic, while when the molecule has one or more electrons unpaired, it will be paramagnetic.

7. The stability of the molecule formed or the strength of bonds between the bonding atoms is determined by bond order.

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

N_b : Number of electrons in bonding molecular orbitals.

N_a : Number of electrons in anti-bonding molecular orbitals.

- Greater the bond order, greater is the stability of the molecule.
- A bond order of +1 indicates that the specie is stable and that the two atoms in a molecule are held together by a single bond. A bond order of +2 indicates that the specie is stable and that the two atoms are united together with a double bond. A bond order of +3 indicates that the specie is stable and that the two atoms are held together by a triple bond.
- Bond order may be fractional and even zero.
- A zero bond order indicates the equal number of bonding and anti-bonding electrons.
- When bond order is zero, the species does not exist.
- A bond order of + 1/2 indicates that the species exists but is unstable, e.g. H_2^+ and He_2^+.
- The bond order of a molecule is directly proportional to its bond dissociation energy and inversely proportional to its bond length. For example,

Molecule	Bond order	Bond length	Bond diss. energy (kJ mol^{-1})
Li_2 (Li—Li)	1	267pm	110
B_2 (B—B)	1	159pm	297
F_2 (F—F)	1	142 pm	158
C_2 (C = C)	2	124pm	607
O_2 (O = O)	2	121 pm	498
N_2 (N ≡ N)	3	110 pm	945
CO ($\overset{-}{C} \equiv \overset{+}{O}$)	3	113pm	1076

Note : We cannot exactly correlate particular values of the bond dissociation enthalpy and distance with a given bond order. Factors such as inter-nuclear and inter-electron repulsion play an important part in determining the observed values of these parameters.

Structures of some Homonuclear Diatomic Molecules

(i) Hydrogen molecule (H_2) :

Total number of electrons in 2H atoms = 1 + 1 = 2

Electronic configuration of H_2 molecule = $\sigma 1s^2$

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

(ii) Hydrogen molecule ion (H_2^+):

Number of electrons in $H_2^+ = 2 - 1 = 1$

Electronic configuration = σ 1s^1

$$\therefore \qquad \text{Bond order } \frac{1}{2}(1-0) = \frac{1}{2}$$

Since the bond order is $\frac{1}{2}$, H_2^+ ion can exist but it is unstable. Further as it has 1 unpaired electron, it is paramagnetic.

(iii) **B_2 :** B_2 is found only in the gas phase ; solid boron is found in several very hard forms with complex bonding, primarily involving B_{12} icosahedra [Structure of B_{12} icosahedron is described in chapter p-Block Elements - I.

B_2 is paramagnetic. The Lewis dot model cannot account for the paramagnetic behaviour of this molecule. The electronic configuration of boron atom shows that it has 5 electrons, hence the molecular orbitals of B_2 molecule have 10 electrons which are distributed in the following manner.

$$KK^*, (\sigma 2s)^2, (\sigma * 2s)^2, (\pi 2P_x)^1\ (\pi 2P_y)^1$$

Note : K indicates first bonding MO and K* antibonding MO, thus KK* is same as $\sigma 1s^2\ \sigma^* 1s^2$.

Thus molecular orbital of B_2 has 6 electrons in bonding and 4 electrons in anti-bonding molecular orbitals.

Thus the bond order of B_2 molecule is calculated as below :

$$\text{Bond order} = \frac{1}{2}\text{[Number of bonding electrons]} - \text{[Number of anti-bonding electrons]}$$

$$= \frac{1}{2}[6-4] = \frac{1}{2} \times 2 = 1$$

The highest energy occupied molecular orbital (HOMOs) of B_2 is π_{2Px} and π_{2Py} .

Note : B_2 is a good example of the energy level shift caused by the mixing of s and p orbitals. In the absence of mixing the σ_{2Pz} orbital is expected to be lower in energy than the π_{2Px} and π_{2Py} orbitals and the resulting molecule would be diamagnetic. However, mixing of orbitals lowers the energy of the σ_{2s} orbital and increases the energy of the σ_{2Pz} orbitals to a higher level than the π_{2Px} and π_{2Py} orbitals, giving the order of energies shown in molecular orbital diagram.

The lowest energy unoccupied molecular orbital (LUMOs) of B_2 molecule is σ_{2Pz}.

(iv) **C_2 :** C_2 is found only in the gas phase. It is not a commonly encountered chemical species (carbon is more stable as diamond, graphite and the fullerenes described in chapter p-block-I).

The electronic configuration of carbon atom shows that it has 6 electrons, hence the molecular orbitals, hence the molecular orbitals of C_2 molecule have 12 electrons which are distributed in the following manner.

$$KK^*, (\sigma 2s)^2, (\sigma * 2s)^2, (\pi 2P_x)^2\ (\pi 2P_y)^2$$

Thus molecular orbitals of C_2 has 8 electrons in bonding and 4 electrons in anti-bonding molecular orbitals. The bond order of C_2 molecule is calculated as below :

$$\text{Bond order} = \frac{1}{2}\text{[Number of bonding electrons]} - \text{[Number of anti-bonding electrons]}$$

$$= \frac{1}{2}[8-4] = \frac{1}{2} \times 4 = 2$$

The simple MO picture of C_2 predicts a doubly bonded molecule with all electrons paired, but with both highest occupied molecular orbitals (HOMOs) having π symmetry. It is unusual because it has two π bonds and no σ-bond.

Note : The acetylide ion, C_2^{2-} , is well known, particularly in compounds with alkali metals (Na_2C_2), alkaline earth metal (CaC_2), and lanthanides. According to the molecular orbital model C_2^{2-} should have a bond order of 3. This is supported by the similar C – C distances in acetylene (C_2H_2) and calcium carbide (CaC_2).

	C – C bond distance (pm)
$HC \equiv CH$	120.5
$Ca^{2+}\bar{C} \equiv \bar{C}$	119.1

(v) Nitrogen (N_2) :

The electronic configuration of nitrogen atom shows that it has 7 electrons, hence the molecular orbitals of nitrogen molecule have 14 electrons which are distributed in the following manner :

$$KK^*, (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$$

Thus the molecular orbital of nitrogen has 10 electrons in bonding and 4 electrons in anti-bonding orbitals. Thus Thus the bond order or the number of bonds in nitrogen molecule may be calculated as below :

$$\text{Bond order} = \frac{1}{2}\ [\text{Number of bonding electron} - \text{Number of anti-bonding electrons}]$$

$$= \frac{1}{2}[10-4] = \frac{1}{2} \times 6 = 3$$

(vi) Oxygen (O_2) :

Oxygen (Z = 8) has the electronic configuration $1s^2 2s^2 2p^4$, so 12 electrons are to be filled in the molecular orbitals of oxygen (leaving aside the electrons of the K shell). These 12 electrons are filled in the following manner :

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

Note that the 11th and 12th electrons in the molecular orbital of oxygen go to $\pi^* 2p_x$ and $\pi^* 2p_y$ orbital (Hund's rule) , it is because of the fact that these two anti-bonding orbitals are of equal energy. Since now there are two unpaired electrons, the oxygen molecule is paramagnetic.

$$\text{Bond order} = \frac{1}{2}\ [\text{Number of bonding electron} - \text{Number of anti-bonding electrons}]$$

$$= \frac{1}{2}[10-6] = 2$$

Hence, the two oxygen atoms in oxygen molecule are linked by a double bond.

(vii) Molecular orbital configuration of O_2^+ :

Number of electrons in $O_2^+ = 16 - 1 = 15$

MO configuration : $KK^*, (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^1 (\pi^* 2p_y)^0$

$$\text{Bond order} = \frac{1}{2}[10-5] = 2\frac{1}{2}$$

Bond order of $+2\frac{1}{2}$ indicates that O_2^+ is more stable than O_2. As O_2^+ has 1 unpaired electrons, it is paramagnetic.

Note : The addition of one or more electrons corresponds to reduction and the removal of one or more electrons is oxidation. The addition of electrons will follow the aufbau principle ; the removal of electrons follows the same rules but in reverse.

MO Electronic Configuration of Diatomic Species having upto 14 electrons :

Molecule or Ion	Total No. of Electron	Electronic Configuration							N_B	N_A	Bond order	Paramagnetic (P) Diamagnetic (D)
		σ 1s	σ*1s	σ 2s	σ*2s	π 2p_x	π 2p_y	σ 2p_z				
H_2	2	2							2	0	1.0	D
H_2^+	1	1							1	0	0.5	P
He_2	4	2	2						2	2	0.0	D
He_2^+	3	2	1						2	1	0.5	P
Li_2	6	2	2	2					4	2	1.0	D
Be_2	8	2	2	2	2				4	4	0.0	D
B_2	10	2	2	2	2	1	1		6	4	1.0	P
C_2	12	2	2	2	2	2	2		8	4	2.0	D
N_2	14	2	2	2	2	2	2	2	10	4	3.0	D
O_2^{2+}	14			(same as N_2)					10	4	3.0	D
N_2^+	13	2	2	2	2	2	2	1	9	4	2.5	P
CN^-	14				(same as N_2)				10	4	3.0	D

MO Electronic Configuration of Diatomic Species having more than 14 electrons :

Molecule or ion	Total No. of Electrons	Electronic Configuration										N_B	N_A	Bond order	Paramagnetic (P) Diamagnetic (D)
		σ 1s	σ*1s	σ 2s	σ*2s	σ 2p_z	π 2p_x	π 2p_y	π* 2p_x	π* 2p_y	σ* 2p_z				
O_2	16	2	2	2	2	2	2	2	1	1		10	6	2.0	P
O_2^+	15	2	2	2	2	2	2	2	1			10	5	2.5	P
NO	15	2	2	2	2	2	2	2	1			10	5	2.5	P
O_2^-	17	2	2	2	2	2	2	2	2	1		10	7	1.5	P
O_2^{2-}	18	2	2	2	2	2	2	2	2	2		10	8	1.0	D
F_2	18	2	2	2	2	2	2	2	2	2		10	8	1.0	D
Ne_2	20	2	2	2	2	2	2	2	2	2	2	10	10	0.0	D

Note : O_2^- : superoxide ion , O_2^{2-} : peroxide ion [Remember as a fact : Bond order of CO^+ is 3.5]

Illustration - 13 *Which of the two peroxide ion or superoxide ion has larger bond length ?*

SOLUTION :

The bond length in a molecule is dependent on bond order. The higher is the bond order, smaller will be the bond length.

Peroxide ion, O_2^{2-}

$$O_2^{2-}: \quad KK^*(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2 (\pi^* 2p_x)^2(\pi^* 2p_y)^2$$

$$\text{Bond order} = \frac{10-8}{2} = 1$$

Superoxide ion, O_2^-

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

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

Bond order of superoxide ion is higher than peroxide ion, hence bond length of peroxide ion is larger.

Illustration - 14 **(a)** *How bond energy varies from N_2^- to N_2^+ and why ?*

(b) *On the basis of molecular orbital theory what is similarity between*

(i) *F_2 and O_2^{2-}* **(ii)** *CO, N_2, NO^+ ?*

SOLUTION :

(a) Bond energy of N_2^+ = Bond energy of N_2^- because bond order is same in both the species. [However, N_2^+ is slightly more stable than N_2^- as antibonding electrons number is higher in N_2^- than in N_2^+.]

(b) **(i)** Both F_2 and O_2^{2-} have same bond order same bond length and are diamagnetic.

(ii) These are isoelectronic species, possess same bond order and same bond length.

Illustration - 15 *Arrange the following compounds in the increasing order of bond length of O – O bond in $O_2[AsF_6]$, O_2, KO_2* and peroxide ion. *Explain on the basis of ground state electronic configuration of dioxygen in these molecules.*

SOLUTION :

$O_2[AsF_6]$ has O_2^+ ion while KO_2 has O_2^- ion (superoxide ion) and peroxide is O^{2-}.

$$\text{E.C. of } O_2 = KK^*\,\sigma(2s)^2\,\sigma^*(2s)^2\,\sigma(2p_z)^2\,\pi(2p_x)^2\,\pi(2p_y)^2\,\pi^*(2p_x)^1\,\pi^*(2p_y)^1$$

$$\text{E.C. of } O_2^+ = KK^*\,\sigma(2s)^2\,\sigma^*(2s)^2\,\sigma(2p_z)^2\,\pi(2p_x)^2\,\pi(2p_y)^2\,\pi^*(2p_x)^1$$

$$\text{E.C. of } O_2^- = KK^*\,\sigma(2s)^2\,\sigma^*(2s)^2\,\sigma(2p_z)^2\,\pi(2p_x)^2\,\pi(2p_y)^2\,\pi^*(2p_x)^2\,\pi^*(2p_y)^1$$

$$\text{E.C. of } O_2^{2-} = KK^*\,\sigma(2s)^2\,\sigma^*(2s)^2\,\sigma(2p_z)^2\,\pi(2p_x)^2\,\pi(2p_y)^2\,\pi^*(2p_x)^2\,\pi^*(2p_y)^2$$

$$\text{B.O. of } O_2 = 1/2\,(10-6) = 2$$

$$\text{B.O. of } O_2^+ = 1/2\,(10-5) = 2.5$$

$$\text{B.O. of } O_2^- = 1/2\,(10-7) = 1.5$$

$$\text{B.O. of } O_2^{2-} = 1/2\,(10-8) = 1$$

Higher is the B.O., smaller is the bond length. Hence, order of O – O bond length is

$$O_2^+ < O_2 < O_2^- < O_2^{2-} \quad \text{i.e.,}$$

$$O_2[AsF_6] < O_2 < KO_2 < O_2^{2-}$$

Note : bond strength $\propto \dfrac{1}{\text{bond length}}$