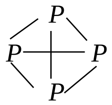
Molecular orbital theory

61. (a)



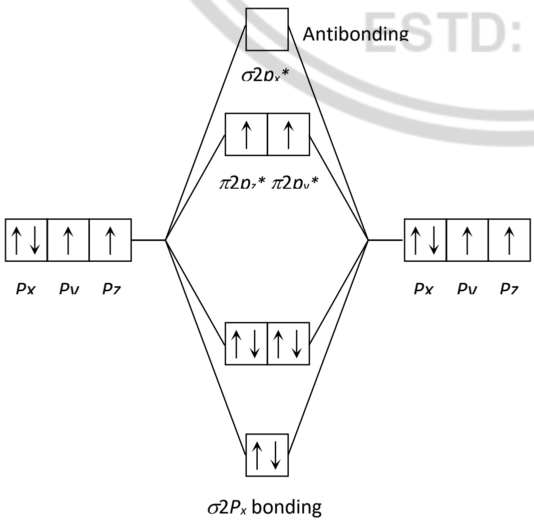
62. **(b) X = 4, Y = 60°**

Word-friendly explanation:
White phosphorus exists as **P_4**, so its **atomicity (number of atoms per molecule) is 4**. The four P atoms form a regular tetrahedron where the **angle between any two P–P bonds at an atom is 60°** .

63. *(a)* $\sigma(1s)^2\ \sigma(1s)^2\ \sigma(2s)^2\ \sigma(2s)^2\ \pi(2p)^4\ \sigma(2p)^1$**

Word-friendly explanation:
N_2 has 14 electrons; N_2^+ has **13 electrons**. Using the MO order appropriate for N_2 (π 2p filled before σ 2p), the highest electron is removed from the σ(2p) orbital, giving the configuration shown in option (a).

64. (c) The paramagnetic property in oxygen came through unpaired electron which can be explained by molecular orbital theory.

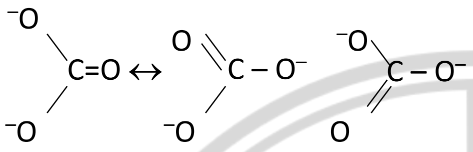


So 2 unpaired of electron present in $\pi\ 2p_y^*$ and $\pi\ 2p_z^*$.

65. (a) Bond order $= \dfrac{\text{Total number of bonds between atoms}}{\text{Total number of resonating structure}}$

$= \dfrac{5}{4} = 1.25$

66. (c) We know that carbonate ion has following resonating structures



Bond order $= \dfrac{\text{Total number of bonds between atoms}}{\text{Total number of resonating structure}}$

$= \dfrac{1+1+2}{3} = \dfrac{4}{3} = 1.33$.

67. (a) $O_2^+(15e^-) = K : K^*(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2$
$(\pi 2p_y)^2(\pi 2p_z)^2(\pi^* 2p_y)^1(\pi^* 2p_z)^0$

Hence, bond order $= \dfrac{1}{2}(10-5) = 2.5$

$N_2^+(13e^-) = KK^*(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2$
$(\pi 2p_y)^2(\pi 2p_z)^1$

Hence, bond order $= \dfrac{1}{2}(9-4) = 2.5$.

68. (a) Electronic configuration of O_2 is
$O_2 = (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2$
$(\pi 2p_x^2 \equiv \pi 2p_y^2)(\pi^* 2p_x^1 \equiv \pi^* 2p_y^1)$

Hence bond order $= \dfrac{1}{2}[N_b - N_a] = \dfrac{1}{2}[10-6] = 2$.

69. (c) Nitrogen form triple bond $N \equiv N$
In which 6 electron take part.

70. (a) As bond order increase bond length decrease the bond order of species are

$= \dfrac{\text{number of bonding electron - Number of } a.b. \text{ electron}}{2}$

For $O_2 = \frac{10-6}{2} = 2$;

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

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

So, bond order $O_2^+ > O_2 > O_2^-$ and bond length are $O_2^+ > O_2 > O_2^-$.

71. (b) $O_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x{}^2 \begin{cases} \pi 2p_y{}^2 \\ \pi 2p_z{}^2 \end{cases} \begin{cases} \pi^* 2p_y{}^1 \\ \pi^* 2p_z{}^1 \end{cases}$

Bond order $= \frac{10-6}{2} = 2.0$

(Two unpaired electrons in antibonding molecular orbital)

$O_2^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x{}^2 \begin{cases} \pi 2py^2 \\ \pi 2pz^2 \end{cases} \begin{cases} \pi^* 2py^1 \\ \pi^* 2pz^0 \end{cases}$ Bond order $= \frac{10-5}{2} = 2.5$

(One unpaired electron in antibonding molecular orbital so it is paramagnetic)

72. (b) Higher the bond order, shorter will be the bond length, thus NO^+ having the higher bond order that is 3 as compared to NO having bond order 2 so NO^+ has shorter bond length.

73. (d) Oxygen molecule (O_2) boron molecule (B_2) and N_2^+ ion, all of them have unpaired electron, hence they all are paramagnetic.

74. (c) Bond order of NO^+, NO and NO^- are 3, 2.5 and 2 respectively, bond energy $\propto$ bond order

75. (a) Paramagnetic property arise through unpaired electron. B_2 molecule have the unpaired electron so it show paramagnetism.

$B_2 \rightarrow \underset{\text{(2 unpaired electron)}}{\sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \pi 2p_x{}^1 = \pi 2p_y{}^1}$

$C_2 \rightarrow \underset{\text{(No unpaired electron)}}{\sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \pi 2p_x{}^2 . \pi 2p_y{}^2}$

$N_2 \rightarrow \underset{\text{(No unpaired electron)}}{\sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \sigma 2p_x{}^2, \pi 2p_y{}^2 \pi 2p_z{}^2}$

$F_2 \rightarrow \underset{\text{(No unpaired electron)}}{\sigma s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x{}^2, \pi 2p_y{}^2, \pi 2p_z{}^2},$

$\pi^* 2p_y{}^2, \pi^* 2p_z{}^2$

So only B_2 exist unpaired electron and show the paramagnetism.

76. (b) $O_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x{}^2 \begin{cases} \pi 2p_y{}^2 & \pi^* 2p_y{}^1 \\ \pi 2p_z{}^2 & \pi^* 2p_z{}^2 \end{cases}$

So two unpaired electron found in O_2 at ground stage by which it shows paramagnetism.

77. (b) Due to greater electron affinity Cl_2 has the highest bond energy.

78. (a) Molecular orbital electronic configuration of these species are :

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

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

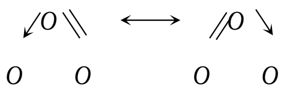
$O_2^{2-}(18e) = \sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \sigma 2p_x{}^2, \pi 2p_y{}^2, \ \pi 2p_z{}^2 \pi^* 2p_y{}^2 \pi^* 2p_z{}^2$

Hence number of antibonding electrons are 7,6,and 8 respectively.

79. (c) Species with unpaired electrons is paramagnetic O_2 has 2 unpaired electrons, O_2^- has one unpaired, O_2^{2-} has zero unpaired electrons, O_2^{2+} has one unpaired.

80. (a) O_2 has 2 unpaired electron while O_2^+ and O_2^- has one each unpaired electrons while O_2^{2+} does not have any unpaired electron.

81. (c) $H-O-O-H$, $O \leftarrow O = O$, $O = O$



Due to resonance in O_3 $O-O$ *bond length will be in b/w* $O=O$ *and* $O-O$.

82. (a) From valency bond theory, bond order in CO, *i.e.* $:\overset{-}{C}\equiv\overset{+}{O}:$ is 3, that of $O=C=O$ is 2 while that of CO_3^{2-} ion is 1.33. Since the bond length increases as the bond order decreases, *i.e.* $CO < CO_2 < CO_3^{2-}$.

83. (c) $N_2 : KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2\pi(2p_y)^2\sigma(2p_z)^2$ (diamagnetic)

$C_2 : KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2\pi(2p_y)^2$ (diamagnetic)

$N_2^+ : KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2\pi(2p_y)^2\sigma(2p_z)^2$ (paramagnetic)

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

84. (d) $NH_3 = 107°, PH_3 = 93°, H_2O = 104.5°$

$H_2Se = 91°, H_2S = 92.5°$