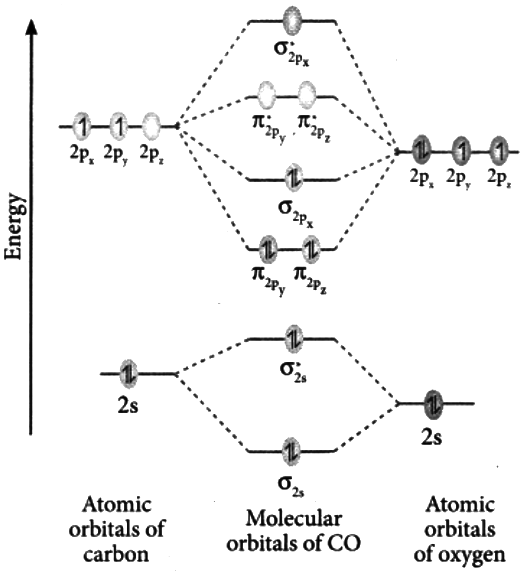
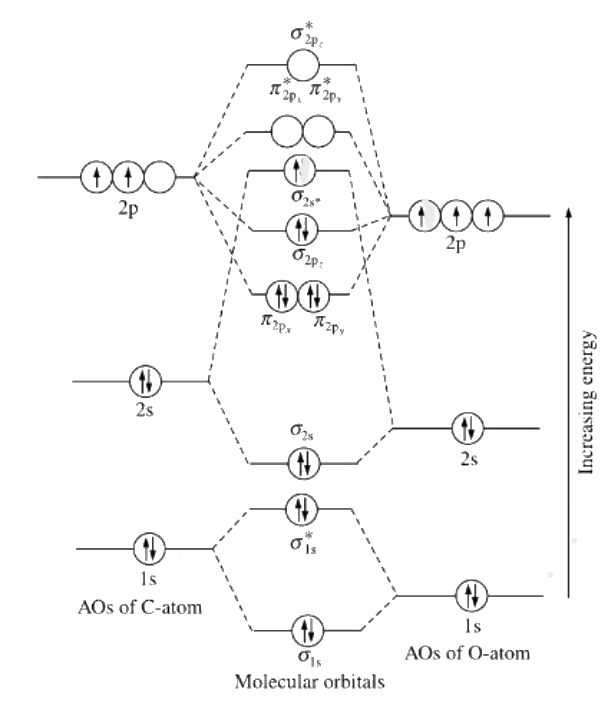
1. Explain p-type and n-type semiconductor with example.
2. Rationalize the bond lengths of CO (1.128Å) and CO+ (1.115Å) with the help of MO diagram. Explain the ligating behaviour of CO.

The bond lengths can be rationalized with the help of bond order. The MO electronic configuration of CO is 1σ2, 2σ2,(1πx2=1πy2), 3σ2, (2πx0=2πy0), 4σ0. Bond order of CO is thus (8-2)/2 = 3

considering the electronic configuration of : In the case of CO+, the increased effective nuclear charge on oxygen, the energy of 2p atomic orbital of oxygen becomes much lower in energy, due to which the energy of 1πpx, 1πpy and 3σ BMOs becomes lower than the energy of 2σ antibonding MO of CO. The MO electronic configuration of CO is 1σ2, (1πx2=1πy2), 3σ2, 2σ1, (2πx0=2πy0), 4σ0. Hence bond order of CO+ is (8-1)/2 = 3.5

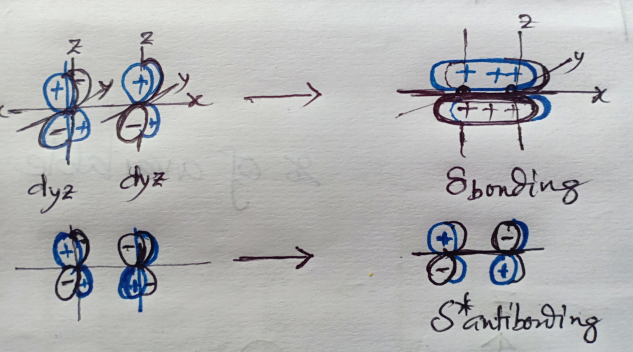
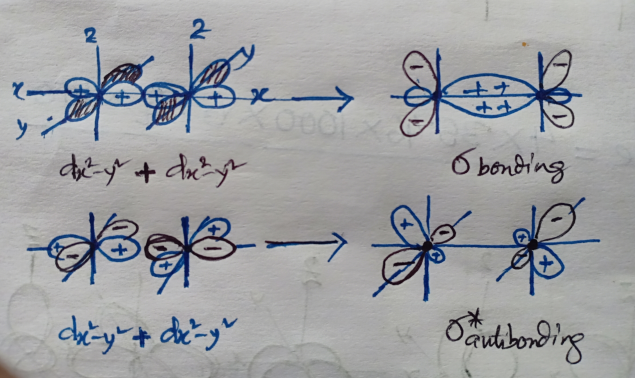
Since bond order of CO is less than CO+ thus it has a longer bond length than CO+.

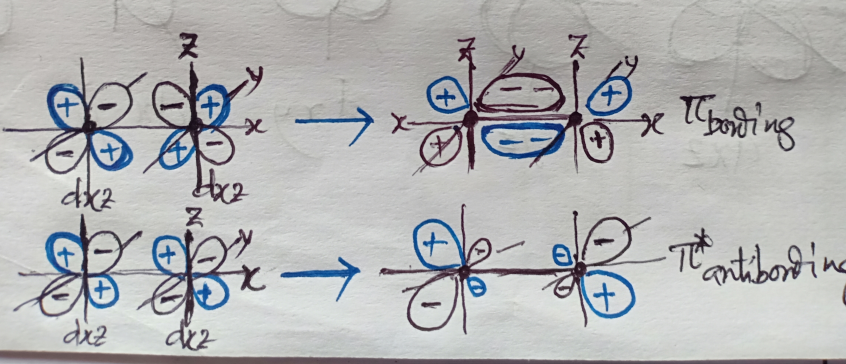
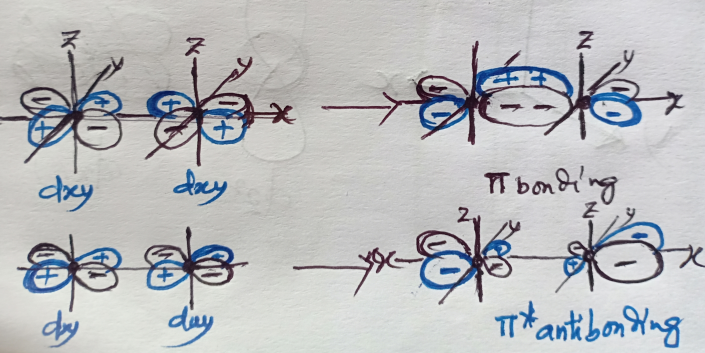
 

**MO of CO+**

1. Assuming X-axis as the bonding axis, predict how many π-MO’s would be formed by d-orbitals of two combining atoms. Give the overlap diagram in each case.

Since X-axis is the bonding axis the two atoms will approach with their d orbitals along the x-axis. So there will be direct overlap of the dx2─y2 that will produce σ MOs. In case of dxy, and dxz, orbitals, two out of four lobes (one +ve and one -ve) from each will overlap partially to give 2 π bonding and 2π anti-bonding molecular orbitals whereas the dyz orbitals will overlap partially to form delta bond. The dz2 orbital here will not form any MO as it cannot come close enough to make an effective overlap.



1. Justify the following bond energy and bond length data from MO theory with diagram.

NO NO+ NO─

Bond energy (kJ mol─1) 627 1047 488

Bond length (Å) 1.15 1.06 1.26

1. What is intrinsic and extrinsic semiconductor?
2. Construct MO energy level diagram of HF molecule and discuss on which atom bonding and antibonding electrons are located?
3. Discuss Frenkel and Schottky defects. Discuss the kind of crystal defect observed when ZnO is heated. State the detectable change.
4. MgSO4 is freely soluble in water where as BaSO4 is almost insoluble. On the other hand MnO is 2000 times more soluble then MgO in water.
5. Explain ion-dipole, dipole-dipole, and dipole-induced dipole interactions mentioning one example in each case.
6. The thermal stability of isomorphus sulphates of Ca, Sr, and Ba with respect to decomposition into the metal oxide MO and SO4 increases in the sequence CuSO4< SrSO4<BaSO4 – explain.
7. Construct the MO diagram of Li2, Li3, and Lin molecules and analyze the related properties.
8. Construct the MO diagram of H2O molecule and calculate its bond order.
9. Compare electronic configuration, paramagnetic and ligational behaviour of CO, and NO molecule.

In CO there is a lone pair of electrons in 3σ( or σ2pz) orbital that can be used for σ donation to a vacant acceptor orbital of metal to form a coordinate bond. Again it can use its vacant 2π (or π\*2px and π\*2py) LUMOs to accept electrons from filled metal orbitals to form π bonds (back bonding). NO also can use its 3σ electron pair to form coordination bond with metal and vacant π\* antibonding orbitals for accepting π electrons to form π back bond. Thus both can act as good ligands to form coordination compounds.

However the ligating strength of CO is greater than that of NO. This is due to two reasons. In CO the 3σ MO is located closer to the C atom but in NO it is closer to the O atom. Lower electro negativity of C makes donation of the 3σ electrons easier. Again presence of an unpaired electron in the 2π MO of NO causes repulsion during accepting electrons from filled metal orbitals to form π back bonds. As a result CO act as a better ligand than NO.

1. Solubility trends of fluorides of alkali metals in water are CsF>RbF>NaF>LiF. But this trend is reverse for iodides.

Polarizing power of cation increases with decrease of size. Again with increasing polarizing power of cation the compound becomes more covalent. On going down a group the size of the cation increases and hence polarizing power decreases. Due to smallest size of Li+ it is most polarizing. Thus LiF is most covalent or least ionic where as CsF is least covalent or most ionic. Hence the trend.

1. With rough energy level diagram, show the ground state electron configuration of (a) H2─, (b)N2, (c) B2─. Find the bond order in each case.
2. Give ground state MO electronic configuration of ClF, CO, and CS.
3. Which of the molecules are expected to be stabilized by (a) addition of electron, (b) removal of electron? (a) NO, (b) C2, (c) O2, (d) CN. Answer by qualitative MO description.
4. Describe in which of the following combinations of the AOs will result in fruitful overlap and formation of MO (consider z axis as the internuclear axis). (a) (3dz2 +3dyz), (b) (3dyz + 3dxz), (c) (2s + 3dx2 – y2)
5. Show the formation of σ, π, and δ bonds by overlap of appropriate d-orbitals of two identical d-bloc atoms (z-axis as the internuclear axis).
6. The energy required to dissociate one O atom from different dioxygen species are reported as (in kJ mol─1): 623, 494, 351, and 205. Correlate these terms with the species O22─, O2─, O2, and O2+. Explain.
7. HF forms stronger H-bonds than H2O. Still ΔHvap of HF is lower than that of H2O. – Explain.
8. Electron affinity of C2 (341 kJmol─1) is much greater than that of N2 ( ─212 kjmol─1) or O2 (42 kjmol─1) – Explain.

Hint: Write MO electronic configuration or draw MO diagram of C2, N2, and O2. If added electron enters in bonding MO then the molecule has higher electron affinity, but if the electron enters in antibonding MO then the molecule will have low electron affinity.

1. How and under what condition an insulator can be converted to semiconductor?

An insulator can be converted into a semiconductor through a process called doping. Doping involves introducing impurities into the crystal lattice of the insulator. This can be achieved by adding specific atoms, such as phosphorus or boron, to the insulator material. When these impurity atoms are added, they can either donate extra electrons (n-type doping) or create "holes" where electrons can move (p-type doping), thus altering the conductivity of the material. By carefully controlling the type and amount of dopants, the insulator can be converted into a semiconductor with specific electrical properties.

1. Draw the MO of HF and HCL and find HOMO, LUMO and the number of non-bonding electrons.
2. CO and N2 are iso-electronic but they differ greatly in donar properties. – Explain.

This is due to nonpolar character of N2. Since the participating AOs originate from identical atoms, the resulting MO energy energy levels do not offer the advantage of σ donation and π acceptance to any significant extent. The LUMO in CO is largely responsible for good π acceptor property─ its low energy and high amplitude on its carbon donor atom allows good overlap with the metal d orbitals. The symmetrical N2 molecule is clearly devoid of this advantage.

1. Explain why liquid oxygen sticks to magnetic pot.

MO electronic configuration of oxygen shows presence of unpaired electrons in its 2π antibonding MOs. This make O2 to be paramagnetic and so O2 in the liquid form gets attracted to magnetic poles.

1. Indicate the type of semiconductor (n-type or p-type) expected to form in the following, (i) As doped Ge, (ii) B doped Si.
2. State the change of bond orders with reasons in the following ionization processes; (i) O2 → O2+ + e, (ii) NO+ + e → NO.
3. Which one has a higher bond order, N2 or NO?
4. What is the magnetic character of the anion of KO2?
5. Why N2+ has a longer bond length than N2 but O2+ has a smaller bond length than O2.

