# Chemistry

# **Topics Under Discussion**

Chemical Bonding, and
 Co-ordination Chemistry

According to Valancy bond theory, oxygen molecule is diamagnetic, but it is found to be paramagnetic.

Also valance bond theory does not explain bond formation in molecular ions like  $0_2^+$ ,  $0_2^-$  etc. An atomic orbital is 3 dimensional region in space around nucleus of an atom where there is maximum probability of finding an electron.

1. What is a molecular orbital? A molecular orbital is the region in space encompassing the nuclei of all the bonded atoms in which there is maximum probability of finding an electron.



2. What are the main features of molecular orbital theory? The main features of molecular orbital theory are Molecular orbitals are formed by the combination of atomic orbitals of comparable energies.

• The number of molecular orbitals formed is equal to the number of atomic orbitals combined.

 When two atomic orbitals combine, they form two molecular orbitals called bonding molecular orbital and anti-bonding molecular orbital.  A bonding molecular orbital has lower energy than combining atomic orbitals and anti bonding molecular orbital has higher energy. Molecular orbitals polycentric. Each molecular orbital can accommodate only two electrons.

3. How are the molecular orbitals formed by LCAO? As per LCAO, atomic orbitals combine to give molecular orbitals in two ways. a) Additive or symmetric overlapping gives bonding molecular orbitals by the addition of two atomic orbitals. b) Subtractive or asymmetric overlapping gives anti-bonding molecular orbitals by the subtraction of two atomic orbitals.

4. Sketch the shapes of bonding and anti-bonding molecular orbitals formed when two s and porbitals, undergo LCAO. 1s+1s  $\rightarrow \sigma$ 1s+ $\sigma$ \*1s  $2s+2s \rightarrow \sigma 2s + \sigma^* 2s$  $2p_7 + 2p_7 \rightarrow \sigma 2p_7 + \sigma^* 2p_7$  $2p_x + 2p_x \rightarrow \pi 2p_x + \pi^* 2p_x$ 



## Diagram showing $\sigma$ 1s and $\sigma$ \*1s



# Diagram showing $\sigma^* 2p_z, \sigma 2p_z, \pi^* 2p_x$ = $\pi^* 2p_y, \pi 2p_x = \pi 2p_y,$ respectively

5. Write the increasing order of energies of molecular orbitals for diatomic molecules with atomic number (Z) > 7.

 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x$ = π2p<sub>y</sub> < π<sup>\*</sup>2p<sub>x</sub> = π<sup>\*</sup>2p<sub>y</sub> < σ<sup>\*</sup>2p<sub>z</sub> 6. Give differences between bonding and anti-bonding molecular orbitals.

Bonding molecular orbital	Anti- bonding molecular orbital
Formed by symmetric combination of atomic orbitals.	Formed by asymmetric combination of atomic orbitals.
Has less energy than the energy of atomic orbitals.	Has more energy than the energy of atomic orbitals.
Favours bond formation.	Does not favour bond formation.
Represented by $\sigma$ , $\pi$	Represented by $\sigma^*$ , $\pi^*$

7. What is bond order? It is one half the difference between the number of bonding electrons and anti-bonding electrons. 8. What is the relationship of bond order with stability of the molecule and bond length?

Higher the bond order, greater is the stability of the molecule and lesser is the bond length. 9. Explain the energy level diagram, bond order and magnetic property of hydrogen molecule. The molecular electronic configuration of hydrogen molecule is  $\sigma 1s^2$ **Energy level diagram for** hydrogen H atom Highing

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# Bond order = $\frac{Nb - Na}{2} = \frac{2 - 0}{2} = 1$

Since there are no unpaired electrons hydrogen molecule is diamagnetic. 10. Explain the energy level diagram and bond order of helium molecule. The molecular electronic configuration of helium molecule is  $\sigma 1s^2$ ,  $\sigma^* 1s^2$ 

Energy level diagram for helium



# Bond order $= \frac{Nb - Na}{2} = \frac{2 - 2}{2} = 0$

# Since bond order is zero Helium (He) molecule does not exist.

11. Explain the energy level diagram, bond order and magnetic property of lithium molecule.

The electronic configuration of lithium molecule is  $\sigma 1 s^2$ ,  $\sigma^* 1 s^2$ ,  $\sigma 2 s^2$ Bond order =  $\frac{Nb - Na}{2} = \frac{4 - 2}{2} = 1$ 

## Energy level diagram for lithium molecule.

Since there are no unpaired electrons, Li molecule is diamagnetic.



12. Explain the energy level diagram, bond order and magnetic property of oxygen molecule. The electronic configuration of oxygen molecule is  $\sigma 1s^2$ ,  $\sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_2^2,$  $\pi 2p_x^2 = \pi 2p_v^2$ ,  $\pi^* 2p_x^1 = \pi^* 2p_v^1$ 

# Bond order = $\frac{Nb - Na}{2} = \frac{10 - 6}{2} = 2$

Since there are unpaired electrons present, oxygen molecule is paramagnetic.

# Energy level diagram for oxygen molecule.



13. What is electron sea model of metallic bond? According to this theory a solid metal consist of a regular array of positive ions(kernels) which are closely packed. The valance electrons move freely in the entire crystal lattice.

Hence metal can be considered as assembly of positive ions immersed in a sea of electrons. Hence the name electron sea

model.



14. How do you explain metallic luster using electron gas theory? When light falls on the fresh surface of a metal, freely moving electrons absorb photons of these radiation and start oscillating. While oscillating they emit radiation that appears as luster.

# **Co-ordination Chemistry**

Na

NaCl, KCl – Simple Salt FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> - Double Salt K<sub>4</sub>[Fe(CN)<sub>6</sub>] - Complex Compound K<sub>3</sub>[Fe(CN)<sub>6</sub>] – Complex Compound

1. What is a co-ordination compound? Give an example. It is a compound where a central metal ion or atom is surrounded by a negatively charged ions or neutral molecules through co-ordinate bonds.

Example:  $K_4[Fe(CN)_6]$ 

## **Central metal ion**

Ligand

K<sub>4</sub>[Fe(CN)<sub>6</sub>] Ionization Co sphere

Co-ordination sphere 2. What is a ligand? Give examples. A ligand is defined as an ion, atom or a molecule capable of donating one or more pairs of electrons to the central metal ion or atom. **Examples: Neutral ligand** H<sub>2</sub>O NO<sub>2</sub>-**Negative ligand** NO<sup>+</sup> **Positive ligand** 

3. What is an ambidentate ligand? Give an example. It is a ligand containing more than one donor atoms but co-ordinate with the metal ion through only one donor atom at a time. Example: M←SCN, M←NCS

## K<sub>3</sub>[Fe(CN)<sub>6</sub>] Anionic complex

## $[Cu(NH_3)_4]SO_4$ Cationic complex

# [Ni(CO)<sub>4</sub>] Neutral complex

Co-ordination Number of a metal ion or atom in a complex is defined as the number of monodentate ligands attached to the central metal ion or an atom in the complex. 4. What are the rules for IUPAC nomenclature of co-ordinate compounds?

a) The cation is named first followed by anion.

b) The number of ligands present is indicated by prefixes di, tri, tetra, penta and hexa to indicate two, three, four, five and six ligands respectively. c) Name of the negative ligand ends in o, name of the positive ligand end in ium and names of the most of neutral ligands remain as such except water (aqua) and ammonia (ammine). d) In anionic complexes the metal ions name end in ate (Fe – ferrate) In cationic and neutral complexes, metal ion or atom name remains the same (Fe – *iron*).

e) The oxidation state of the central ion or atom is expressed in Roman numerals in brackets after the name of the metal without a gap.

 $K_3[Fe(CN)_6]$ Number of ligands (6) hexa Name of ligand cyano Name of metal ion ferrate Oxidation number (III) 3(+1)+x+6(-1) = 03+x-6 = 0x = 6 - 3 = 3potassium hexacyanoferrate(III)

 $[Co(NH_3)_4(H_2O)CI]CI_2$ Number of ligands(4) tetra Name of ammonia ammine Na Name of water aqua Name of chlorine chloro Name of metal ion cobalt Oxidation number(x-1-2= 0) (III) tetraammineaquachlorocobalt(III) chloride 5. Write the IUPAC name of the following complexes.  $K_4[Fe(CN)_6]$ potassium hexacyanoferrate(II)  $K_3[Co(NO_2)_6]$ potassium hexanitrocobaltate(III)  $[Cr(H_2O)_6]Cl_3$ hexaaquachromium(III) chloride

[Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub> tetraamminecupper(II) sulphate [Ni(CO)<sub>4</sub>] tetracarbonylnickle(0) [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>] diamminetetrachloroplatinum(IV) 6. What is a complex cation? Give an example. It is a cation where in central metal ion is surrounded by ligands which carry net positive charge.  $[Cu(NH_3)_4]^{2+}$ 

7. What is an anionic complex?
Give an example.
It is coordination compound containing a complex anion.

Example:  $K_4[Fe(CN)_6]$ 

8. What is ionization isomerism? Give an example. When the two complex compounds have the same molecular formula but produce different ions when dissolved in water are said to exhibit ionization isomerism. Examples: [Co(NH<sub>3</sub>)<sub>5</sub>Br]SO<sub>4</sub> [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]Br

9. What is linkage isomerism? Give an example. **Complexes with the same molecular** formula but different mode of attachment of the ligand to the central metal ion are said to exhibit linkage isomerism. Ex. [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl<sub>2</sub>  $[Co(NH_3)_5ONO]Cl_2$ 

10. What is hydrate isomerism? Give an example. **Co-ordination compounds** having same molecular formula but different number of molecules of water as ligands or molecules of hydration are said to exhibit hydrate isomerism. Ex:  $[Cr(H_20)_6]Cl_3$ ,  $[Cr(H_20)_5Cl]Cl_2.H_2O$  11. Write the postulates of Werner's theory. The postulates of the Werner's theory are a) In the co-ordination compound a metal atom has two types of valencies called primary valency(ionsable) and secondary valency(non ionsable). b) Primary valency is equal to its oxidation state and it is satisfied by negative ions present in the molecule. c) Secondary valency is equal to its co-ordination number and it is satisfied by negative ions or neutral molecules.

d) Secondary valencies of a metal are arranged in space to give definite geometrical shape to the complex depending on the number of ligands. 12. What is EAN? Calculate EAN in  $K_4[Fe(CN)_6]$ . EAN is defined as the total number of electrons present with central metal ion or atom including those donated by the ligands.

It is given by EAN = Z-X+Y **Z** is atomic number of central metal ion. X is the number of electrons lost by the central metal atom. Y is number of electrons gained from the ligands.

### **Example:**

# $ln K_4[Fe(CN)_6],$

## Z=26 X=2 Y=2x6 = 12

Na

EAN = 26-2+12 = 36

**13. State EAN rule.** A metal atom or ion continues to accept electron pairs from the ligands till the total number of electrons present around the metal ion in a complex becomes equal to the atomic number of the next noble gas atom.

14. Calculate EAN in [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>. **Does this complex satisfy EAN** rule? Here, Z=29, X=2, Y=2x4=8 EAN = 29 - 2 + 8 = 35EAN ≠ 36 (atomic number of Kr) Hence, the complex does not satisfy EAN rule.

15. By applying valence bond theory explain hybridization and geometrical shape of cuprammonium ion. Atomic number of Cu 29 Ground state E.C of Cu[Ar]3d<sup>10</sup>4s<sup>1</sup> E.C of Cu<sup>2+</sup> [Ar]3d<sup>9</sup>

When the NH<sub>3</sub> ligand approach Cu<sup>2+</sup> ion electron in the 3d orbital transferred to unhybridized 4p orbital against the Hund's rule.

Hence one 3d orbital, one 4s orbital and two 4p orbital undergo dsp<sup>2</sup> hybridization. These hybrid orbitals of cupric ion overlap with filled orbitals of nitrogen present in NH<sub>3</sub> to form four co-ordinate bonds. Hence shape of the complex is square planar. Since the complex contains unpaired electrons it is paramagnetic.

16. By applying valence bond theory explain hybridization and geometrical shape of ferricynide ion. Atomic number of Fe 26 Ground state E.C of Fe [Ar]3d<sup>6</sup>4s<sup>2</sup> Electronic configuration of Fe<sup>2+</sup>[Ar]3d<sup>6</sup>

When the CN<sup>-</sup> ligand approach Fe<sup>2+</sup> ion electron in the 3d orbital paired up against the Hund's rule.

Hence two 3d orbital , one 4s orbital and three 4p orbital undergo d<sup>2</sup>sp<sup>3</sup> hybridization. These hybrid orbitals of Fe<sup>2+</sup> ion overlap with filled orbitals of nitrogen present in CN<sup>-</sup> to form six co-ordinate bonds. Hence shape of the complex is octahedral. 1 ↓ 1↓ **1** ↓