B.Sc Part-II, Group-B.-3

Valence bond theory approach for complex Compound [Contract]

Paper-III

[Rest Part]

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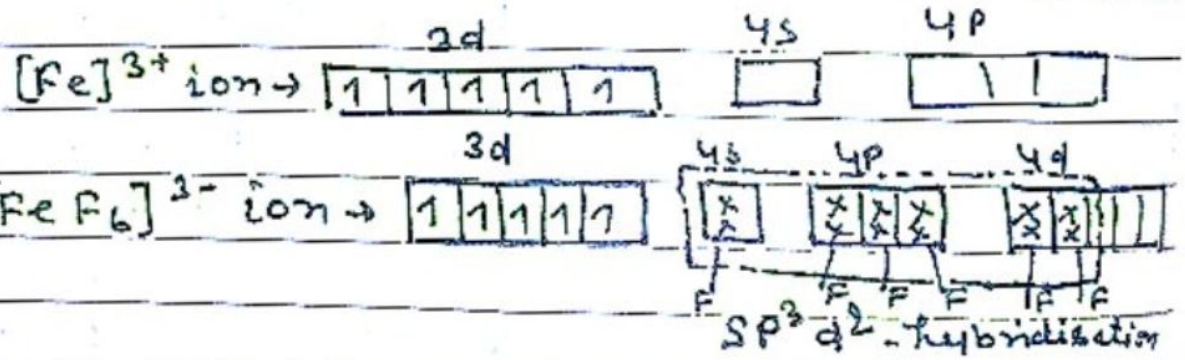
Lecture Notes Series :-

Valence bond theory [Rest Part]

In the formation of $[FeF_6]^{3-}$, when $6F^-$ ion approach to ferric ion pairing of electrons does not take place [because F^- ion is a weak ligand) in this way no empty orbital is available in 3d-orbitals for hybridisation. Hence two empty orbitals of 4d orbitals are involved in hybridisation (ie an example of outer complex) and six sp^3d^2 hybrid orbitals are available to form $[FeF_6]^{3-}$ complex ion as shown below.



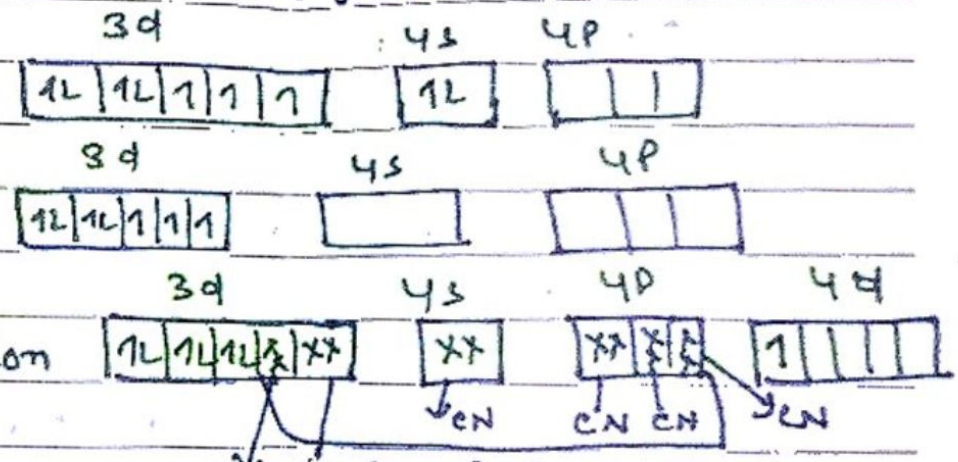
sp^3d^2 hybridisation - octahedral outer orbital complex [Paramagnetic) [Five electrons unpaired]

Since in this complex there are five unpaired electrons hence it is highly paramagnetic. Magnetic moment corresponds to five unpaired electrons ($\mu_{eff} = 5.7 - 6.0$ BM)

The examples of such complexes are $[CoF_6]^{3-}$, $[Fe(NH_3)_6]^{2+}$ etc

It is very interesting to note that the formation of $[Co(CN)_6]^{4-}$. In this case after pairing of electrons only one empty d-orbitals is available and one 3d-orbitals is half field. The unpaired electron is promoted to 4d-orbitals. In this way low complex is formed with paramagnetic character

The inner and outer orbital complexes can be distinguished by magnetic measurements.



d^2sp^3 hybridisation - octahedral, paramagnetic.

One electron of 3d-orbitals is promoted to higher energy level [4d] unpaired electrons

Outer orbital complexes are more reactive or labile and consequently ligands may be substituted easily but the inner orbital complexes are sometimes called inert or non labile and substituent of ligand is fairly difficult.

(ii) Square Planar Complexes :-

It is evident that in transition metal atoms of the configuration $3d^7$ to $3d^{10}$ are capable of forming 4-co-ordination complexes which may have square planar (dsp^2) or tetrahedral (sp^3) str. depending upon the mode of hybridisation. Since the d-electrons can not be accommodated in the lower triplet of levels. Consequently such metal atoms are not capable of forming inner orbitals octahedral complexes unless other changes in electron levels also occurs.

Let us consider the formation of $[Ni(CN)_4]^{2-}$ complex ion.

The electronic configuration of nickel atom is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$ and Ni^{2+} ion has $3d^8$ electrons. When 4 CN^- ions approach to Ni^{2+} ion pairing of electrons takes place. In this way all the 8 electrons in 3d-orbitals are paired and one empty 3d-orbital is available for dsp^2 hybridisation and $[Ni(CN)_4]^{2-}$ complex ion is formed which is shown below

	3d	4s	4p
Ni atom →	1L 1L 1L 1 1	1L	
Ni^{2+} ion →	1L 1L 1L 1 1		
$[Ni(CN)_4]^{2-}$ →	1L 1L 1L 1L ↑↓	↑↓	↑↓ ↑↓

CN CN CN CN

dsp^2 hybridisation

- Square planar - diamagnetic