Valence – Bond – Theory L. Pauling & J.L. Slater

Valence-bond Theory was proposed by Pauling in order to explain the formation of Co-ordination Compounds. This theory is based up on the revolutionary idea of Hybridisation Following are the main points of this theory.

(i) The Central metal ion in the Complex makes available a number of empty Orbitals for the formation of Co-ordinate bonds with the ~~Central~~ Suitable ligands.

The number of empty Orbitals made available for the purpose, gives the Co-ordination number of the Central ion.

(ii) The empty Orbitals of metal ion hybridise (i.e, s, p and d) to give an equal number of new orbitals of equivalent energy Called hybride Orbitals.

(iii) Each ligand has at least one σ-orbital Containing a lone pair of electron.

(iv) The empty hybride Orbitals of metal ion over lap with filled σ-orbitals of the ligand forming ligand-me Co-ordinate bond, the number of empty orbitals made available by Central ion.

The d-orbitals involved in the hybridisation may be $d(x^2-y^2)$, dz^2 (inner) or dxy and dx^2 in the Case of outer

) The non bonding metal electrons occupy the inner d-orbitals, which do not participate in hybridisation.

(vii) A substance which does not contain any unpaired electron is not attracted by the magnet; it is said to be diamagnetic.

On the other hand a substace which contains one or more unpaired electron is attracted by the magnetic field. It is said to be paramagnetic, knowing this, it is possible to predict the type of hybridisation involving during the formation of complex and also its Geometry.

The V.B.T. in some complexes is illustrated below:—

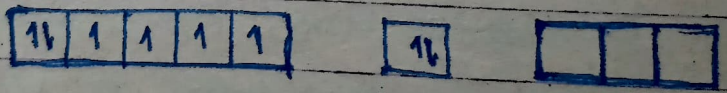
(i) Octahedral Complexes: →

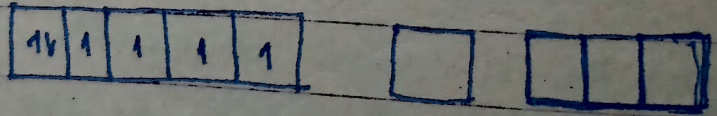
Octahedral complexes are the result of sp^3d^2 (outer) or d^2sp^3 (inner) orbital hybridisation.

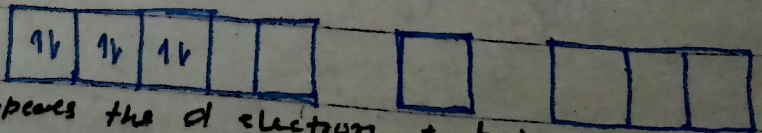
(a) Ferrocyanide ion $[Fe(CN)_6]^{-4}$ →

In this complex iron is as Fe^{+2} whose valence shell configuration is written as (b) in the diagram.

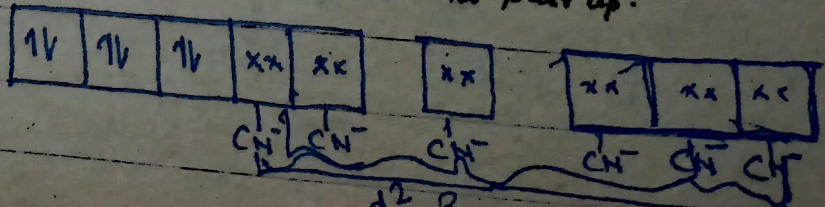
$_{26}Fe \longrightarrow 1s^2 2s^2p^6 3s^2p^6d^6 4s^2$

(a) Fe atom — 

(b) Fe^{+2} " — 

(c) Fe^{+2} in $[Fe(CN)_6]^{-4}$ — 

CN^- is strong ligand so it impeses the d electron to pair up.

(d) $[Fe(CN)_6]^{-4}$ → 

d^2sp^3 hybridisation.

Valence bond diagram showing the formation of octahedral complex, $[Fe(CN)_6]^{-4}$ complex ion involving d^2sp^3 hybridisation.

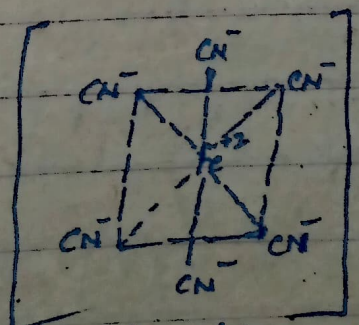
As the six (6) ligands approaches towards central metal ion (Fe^{+2}), the energy thus made available forces to the pairing of unpaired electrons in 3d orbitals by rearranging them, it is shown at c.

~~Thus four unpaired electron becomes~~

Thus out of four unpaired electrons, two becomes paired and two 3d orbital becomes vacant, which are used for hybridisation with one 4s orbital and three 4p orbitals. to give six equivalent d^2sp^3 hybrid orbitals. these hybride orbitals which are directed towards 6 (six) corners of a regular octahedron, accept 6 electron pairs denoted by $6CN^-$ ligands and thus form $[Fe(CN)_6]^{-4}$ as shown at d.

Since the complex is result of d^2sp^3 hybridisation. It has one octahedral shape as shown in figure.

Since there is ~~two~~ no unpaired electron in the complex so, it is diamagnetic.



From the valence bond diagram it is evident that inner d-orbitals have been used in the hybridisation. So complex is called inner orbital complex.