

VALENCE BOND THEORY:

This theory was proposed by L. Pauling in 1930's.
According to this theory:

- (I.) Metal atom or ion under the influence of ligands can use its $(n-1)d$, ns , np or ns , np , nd orbitals for hybridisation to form a set of equivalent energy hybrid orbitals of definite geometry.
- (II.) Hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.
- (III.) Hybridisation of empty orbitals depends upon the nature of metal and nature of approaching ligand.
- (IV.) When d -orbitals of $(n-1)$ shell are used, these are known as inner orbital complex, they are formed due to strong field ligands or low spin ligands and hybridisation such as d^2sp^3 , dsp^2 and so on.
- (V.) When outer d -orbital are used in bonding, the complexes are called outer orbital complexes. They are formed due to weak field ligands or high spin ligands and hybridisation such as sp^3d^2 , sp^3d , sp^3 and so on.

Co-ord. No.	Hybridisation	Shape	Complex Type
4	sp^3	Tetrahedral	Outer orbital complex
4	dsp^2	Squa. Planer	Inner orbital complex
5	sp^3d	Tri. bipyramid	outer orbital complex
6	sp^3d^2	Octahedral	outer orbital complex
6	d^2sp^3	Octahedral	Inner orbital complex

* Application:

- Generally applicable to predict the geometry of complex and also knowing magnetic behaviour of complexes.

Coordination No. 06.

- | | |
|--|--|
| • d^2sp^3 | • sp^3d^2 |
| • due to strong field ligands. | • due to weak field ligands. |
| • inner orbital complex | • outer orbital complex |
| • octahedral geometry | • octahedral geometry |
| • low spin complex | • high spin complex |
| • paramagnetic / diamagnetic | • paramagnetic / diamagnetic |
| • Magnetic momentum
(μ) = $\sqrt{n(n+2)}$ BM. | • Magnetic momentum
(μ) = $\sqrt{n(n+2)}$ BM. |

* NOTE:

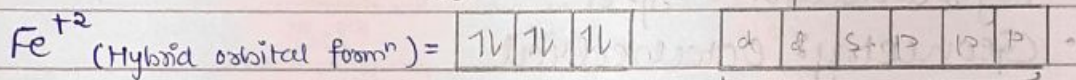
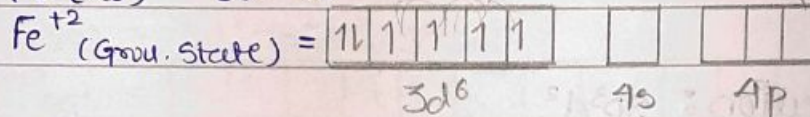
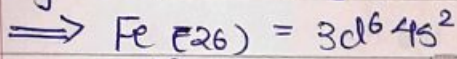
- Generally, carbonyl, cyano, acts as strong field ligand.
- In case of 4d and 5d series of transition metals, all ligands acts as strong field ligands
- H_2O , F^- , Cl^- , Br^- all acts as a weak field ligand.

*NOTE:

- NH_3 (amire) acts as a strong field ligand but with Fe it acts as a weak field ligand.
- In case of Cobalt (Co) all ligands are strong field ligands.

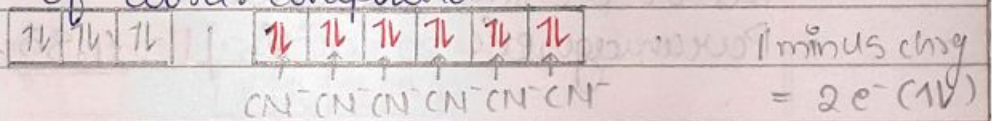
1.) Six coordinated complexes (strong field unidentate lig.):

- eg: $\text{K}_4[\text{Fe}(\text{CN})_6]$;



$3d^6$ No. of d^2sp^3 hybrid orbital

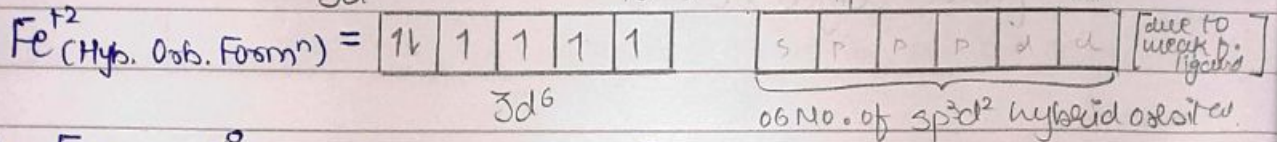
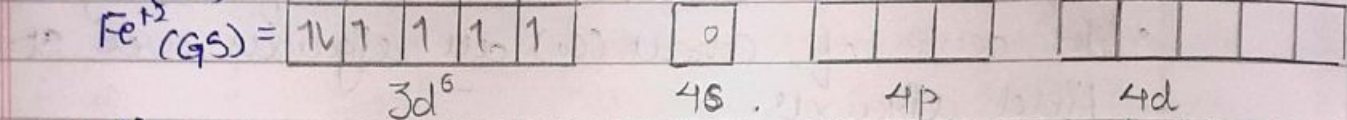
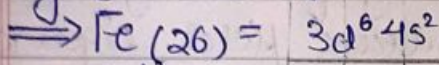
∴, Formation of coord. compound:



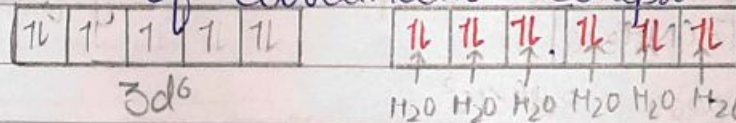
- Because of the presence of strong field ligand, electrons get paired up and provide two vacant d-orbital.
- As inner 'd' orbitals are involved in hybridisation, hence it is an inner orbital complex.
- All electrons are paired ∴, complex will be diamagnetic in nature. ∴, $\mu = 0$
- It is a low spin complex.
- Hybridisation: d^2sp^3
- Geometry: Octahedral.

2) Six coordinated complexes (weak field unidentate ligand):

eg: $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$:



∴, Formation of coordination comp:



- Hybridisation: sp^3d^2
- Geometry: Octahedral
- High spin complex
- Outer orbital complex
- Paramagnetic ∴, $\mu = 4.85$.

3) Six coordinated complexes (strong field unidentate lig.):

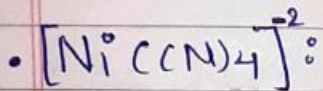
eg: $[\text{Ru}(\text{H}_2\text{O})_6]^{+2}$

→ here, Ru (Ruthenium) is 4d series element. Hence, H₂O acts as a strong field ligand.

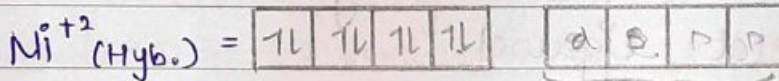
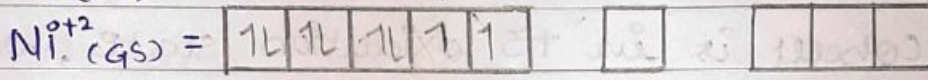
- Hybridisation: d^2sp^3
- Geometry: Octahedral
- Low spin complex
- Inner orbital complex
- Diamagnetic ∴, $\mu = 0$.

4.) Four coordinated complexes:

- | | |
|---|---|
| <ul style="list-style-type: none"> • dsp^2 • inner orbital complex • square planar • low spin complex • paramagnetic or diamagnetic | <ul style="list-style-type: none"> • sp^3 • outer orbital complex • tetrahedral • high spin complex • paramagnetic or diamagnetic |
|---|---|

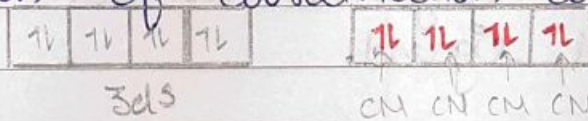


$\Rightarrow Ni^{(28)} = 3d^8 4s^2$

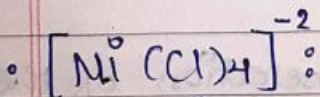


04. No. of dsp^2 hybrid orbital.

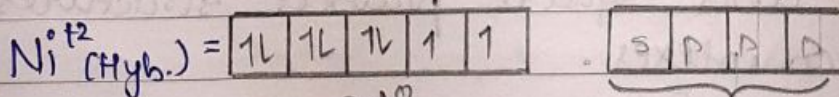
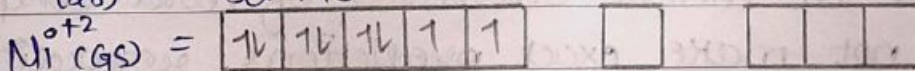
∴ Formation of coordination comp:



- Hybridisation: dsp^2
- Geometry: Square planar
- Low Spin complex
- Inner orbital complex
- Diamagnetic ∴ $\mu = 0$.

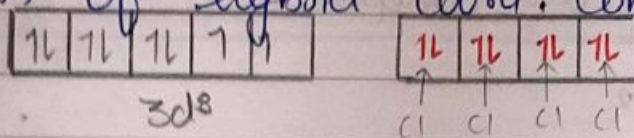


$\Rightarrow Ni^{(28)} = 3d^8 4s^2$



04. No. of sp^3 hybrid orbital.

∴, Formation of hybrid coord. comp:



- Hybridisation : sp^3
- Geometry : tetrahedral
- outer orbital complex
- High spin complex
- Paramagnetic ∴, $\mu = 2.85$

* NOTE:

- when cobalt is in +3 oxidation state, water, ammonia and oxalate $\text{C}_2\text{O}_4^{2-}$ ligands all acts as a strong field ligand. *homonuclear disp*
- Ammonia acts as a weak field ligand with iron, nickel and manganese but with cobalt it acts as a strong field ligand.

* Limitations:

- 1.) It involves number of assumptions.
- 2.) It does not give quantitative interpretation of magnetic data.
- 3.) It does not explain the colour exhibited by coordⁿ compound.
- 4.) It does not give quantitative interpretation of thermodynamics or kinetic stabilities of coordⁿ compounds.
- 5.) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- 6.) It does not distinguish between weak and strong ligand.

★ Solve intext questions for practise ★