

Engineering Chemistry UNIT-1-A-ii

**INTRODUCTION TO ENGG. CHEMISTRY
PART A: i) ATOMS TO MOLECULES TO MATERIALS
FOR ENGINEERS-ii. Co-Ordination complexes**

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To rationalize how the shapes of atomic orbitals are transformed into the orbitals occupied in covalently bonded species,

we need the help of two bonding theories:

Valence Bond (VB) Theory

Molecular Orbital (MO) Theory

VALENCE BOND THEORY [text]

Developed in 1927 by HEITLER and LONDON

**For maximum electron density and overlapping
i.e. stable bond formation-**

- i) The electrons should have opposite spins and**
- ii) The greater overlapping of the electron clouds.**

VALENCE BOND THEORY [text]

Linus Pauling and J.C. Slater extended this theory:

a) Extent of overlapping of the electron wave functions determine the strength of a bond

[maximum overlap=strongest bond]

b) Out of two orbitals of identical stability or energy the one with more directionally concentrated would form a stronger bond.

VALENCE BOND THEORY [text]

P-2

Linus Pauling and J.C. Slater extended this theory:

a) Extent of overlapping of the electron wave functions determine the strength of a bond

[maximum overlap=strongest bond]

b) Out of two orbitals of identical stability or energy the one with more directionally concentrated would form a stronger bond.

c) s-spherically symmetrical

d) The direction of bond forming orbitals will decide the direction. e.g. $P_x - P_x$ overlap will be in x direction.

e) When a bond is formed along x-direction, P_y , P_z orbitals wil remain as it is.

- In order for a covalent bond to form between
- two atoms, **overlap** must occur between the orbitals containing the valence electrons.
- The **best overlap** occurs when two orbitals are allowed to meet “**head on**” in a straight line.
- When this occurs, the atomic orbitals merge to form a single bonding orbital and a
- “**single bond**” is formed, called a **sigma (σ) bond**.

MOLECULAR SHAPES:VALENCE BOND THEORY (VBT)

P-2

Valence Bond Theory:

- **H₂ forms due to overlap of two 1s orbitals.**
- **F₂ : Electron densities from p-subshell electrons overlap to produce a bond in F₂.**
- **CH₄: The 1s orbital of hydrogen must overlap with the 2s and 2p orbitals of carbon.**

LIMITATIONS of VALENCE BOND THEORY [text]

VBT doesn't explain :

a] the formation of coordinate bond

**b] The formation of odd electron molecules
e.g. H_2^+ , NO, O_3 etc. where no electron
pairing takes place.**

c] the paramagnetic nature of Oxygen.

**d] structure of molecules involving resonance
and hybridization.**

MOLECULAR ORBITAL THEORY

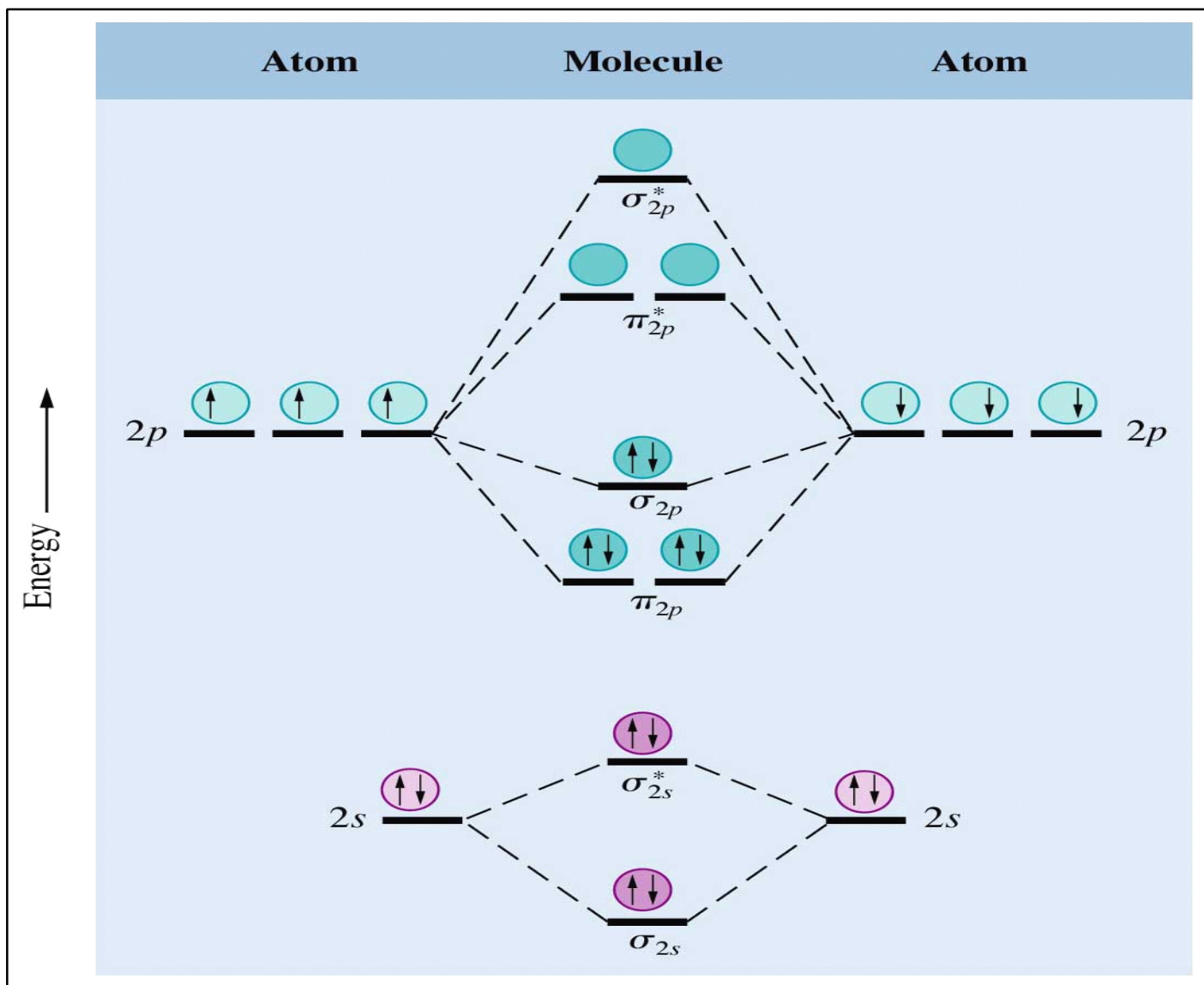


Fig. 10.34 MO Diagram of N_2

Valence Bond Theory for Complex ion or Coordination Compounds.

It is necessary to understand the some important terms used in the study of inorganic compounds. These are discussed here.

1.Ligands The neutral molecules or ions which are attached with the central metal atom are called ligands.

⑥ Ligand acts as a donor partner. The ligands are arranged round the metal ion inside the first sphere of attraction in perfect geometry.

2.Coordination number It is the total number of atoms of the ligands, that can coordinate to central metal ion.

3.Coordination sphere The central metal ion and the ligands that are directly attached to it enclosed in a square bracket are called coordination sphere.

Valence Bond theory (V.B.T)

1. The central metal atom or ion in the complex makes available an adequate number of empty orbitals for the formation of coordination compound with suitable ligands. The number of empty orbitals made available for the purpose is equal to the coordination number of the central atom or ion.
2. Hybrid orbital: The atomic orbitals (s , p and d) of the metal hybridise to give an equal number of new orbitals of equivalent energy called hybrid orbitals.
3. The d orbitals involved in the hybridisation may be inner $(n-1)$ or the outer (n) orbitals.
4. Each ligand has at least one orbital containing a lone pair of electrons.
5. The empty hybrid orbitals of metal ion overlap with the orbitals of ligands to form metal ligand bonds ($M \leftarrow L$).

Table. 1.2: Hybridisation and shapes of complex ions or molecules.


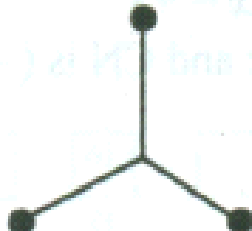
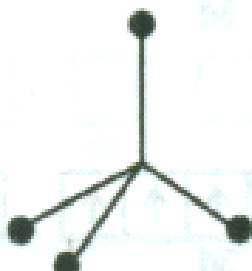
| S.No. | Hybridised orbital | Bond angle | Molecular Geometry | Examples |
|-------|--------------------|------------------|---|------------------------------------|
| 1. | sp | 180° |  <p>Linear</p> | $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$ |
| 2. | sp^2 | 120° |  <p>Plane Triangle</p> | $[HgI_3]$ |
| 3. | sp^3 | $109^\circ. 28'$ |  | $[Ni(CO)_4]$, $[Zn(NH_3)_4]^{+2}$ |

Table. 1.2: Hybridisation and shapes of complex ions or molecules.


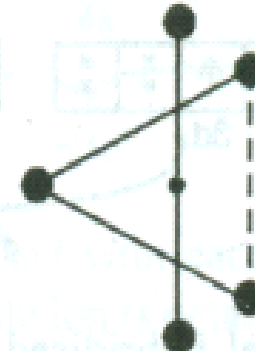
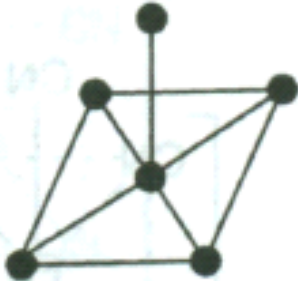
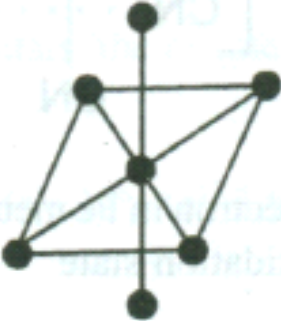
| S.No. | Hybridised orbital | Bond angle | Molecular Geometry | Example |
|-------|--------------------|----------------------------|--|---|
| 4. | dsp^2 | 90° |  <p>Square Planar</p> | $[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$ |
| 5. | dsp^3 | 120° and 90° |  <p>Trigonal bipyramidal</p> | $[Fe(CO)_5]$, $[CuCl_5]^{3-}$ |

Table. 1.2: Hybridisation and shapes of complex ions or molecules.

| S.No. | Hybridised orbital | Bond angle | Molecular Geometry | Example |
|-------|-----------------------|------------|---|--------------------------------------|
| 6. | sp^3d | 90° |  <p>Square Pyramidal</p> | $[SbF_5]^{2-}$, $[IF_5]$ |
| 7. | d^2sp^3 , sp^3d^2 | 90° |  <p>Octahedral</p> | $[Fe(CN)_6]^{3-}$, $[Fe(F)_6]^{3-}$ |

Applications of V.B.T

1. $[\text{K}_3\text{Fe}(\text{CN})_6]$ or $[\text{Fe}(\text{CN})_6]^{3-}$

Fe = 26

The atomic number of Fe = 26

Atomic configuration of Fe $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

Oxidation state of Fe in $[\text{Fe}(\text{CN})_6]^{3-}$ is

$$x + 6(-1) = -3$$

$$x = +3$$

[Here oxidation number of Fe is x and CN is (-1)]

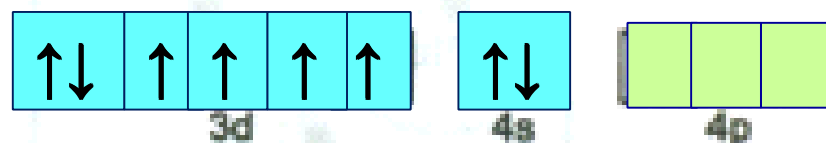
Now Fe is in **(+3)** oxidation state.

[Here oxidation number of Fe is x and CN is (-1)]

Now Fe is in $(+3)$ oxidation state.

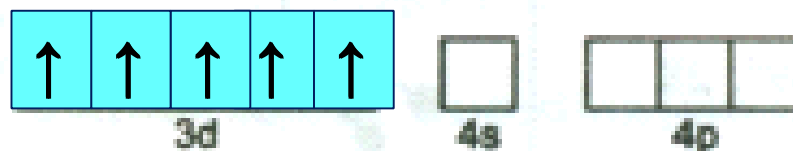
Fe is in G.S

Fe = 26

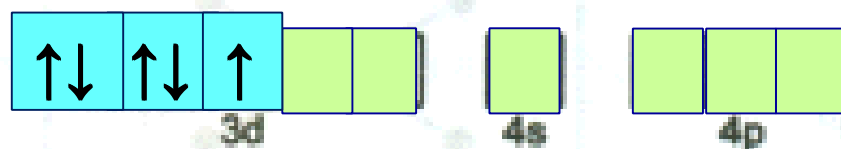


Fe is in $(+3)$ O.s

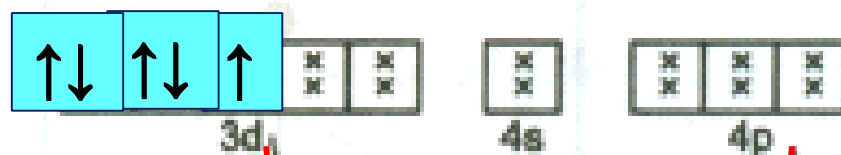
(+3)



Due to influence of strong ligand CN, the rearrangement of Fe electrons takes place.



After hybridisation on filling the electrons of CN in empty orbitals of Fe metal.



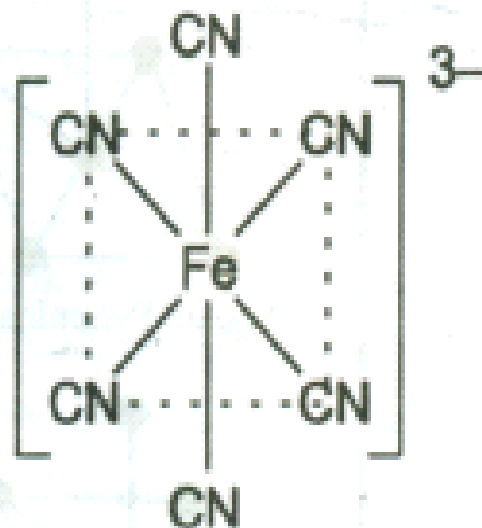
$d^2s p^3$

paramagnetic

Two d , one s and three p orbital hybridised with each other to form $[\text{Fe}(\text{CN})_6]^{3-}$, therefore hybridisation is d^2sp^3 and the shape of the molecule is octahedral.

$d^2s p^3$

$[\text{Fe}(\text{CN})_6]^{3-}$



paramagnetic

There is presence of unpaired electron in Fe metal orbital, the magnetic behaviour is paramagnetic
G.S \Rightarrow ground State, O.S \Rightarrow oxidation state

2. **$K_4 [Fe(CN)_6]$** or $[Fe(CN)_6]^{4-}$ **$[Fe(CN)_6]^{4-}$**

The atomic number of Fe = 26

Atomic configuration of Fe, $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

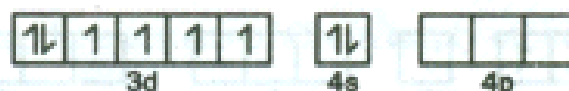
Oxidation state of Fe in $[Fe(CN)_6]^{4-}$ is

$$x + 6(-1) = -4, x = +2$$

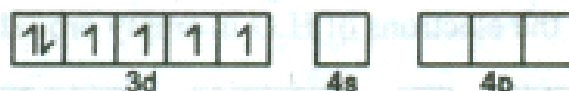
(Here oxidation number of Fe is x and CN is (-1))

Now Fe is in **(+2)** oxidation state

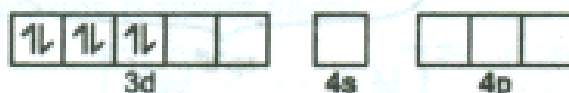
Fe is in G.S



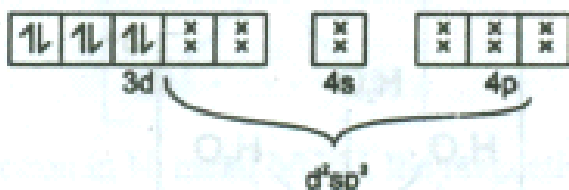
Fe is in (+2)O.S



Due to influence of strong ligand CN, the rearrangement of Fe electrons takes place.



After hybridisation on filling the electrons of CN in empty orbitals of Fe metal.

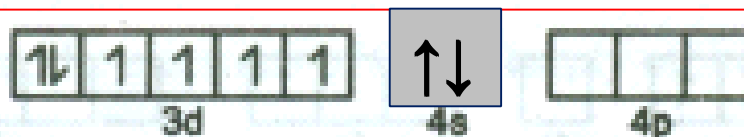




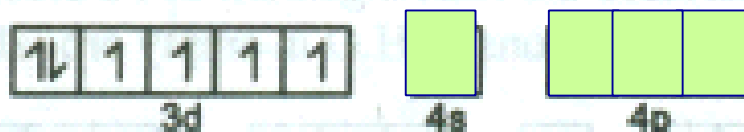
(Here oxidation number of Fe is x and CN is (-1))

Now Fe is in **(+2)** oxidation state

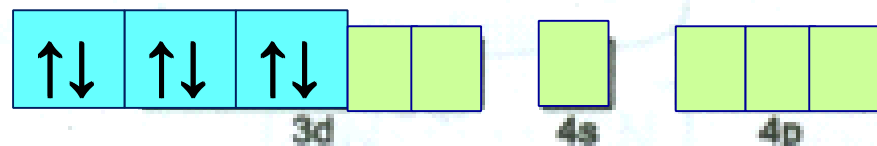
Fe is in G.S



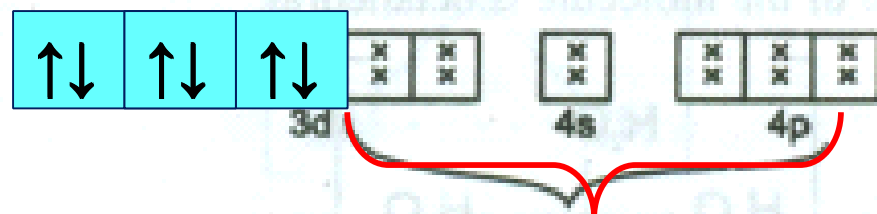
Fe is in (+2)O.S



Due to influence of strong ligand CN, the rearrangement of Fe electrons takes place.



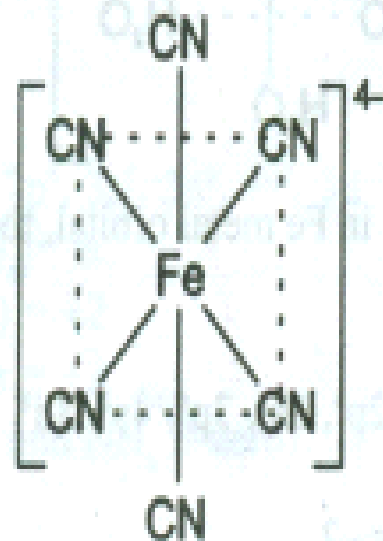
After hybridisation on filling the electrons of CN in empty orbitals of Fe metal.



$d^2s p^3$

diamagnetic

Two *d*, one *s* and three *p* orbitals hybridised with each other to form $[\text{Fe}(\text{CN})_6]^{3-}$, therefore hybridisation is d^2sp^3 and the shape of the molecule ion is octahedral.



diamagnetic

There is no unpaired electron in Fe metal orbitals, the magnetic behaviour is diamagnetic.

3. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

Fe = 26

The atomic number of Fe = 26

Atomic configuration of Fe, $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

Oxidation state of Fe in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is

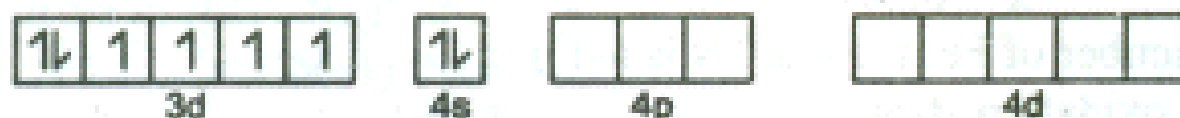
$$x + 6(0) = (+3)$$

$$x = +3$$

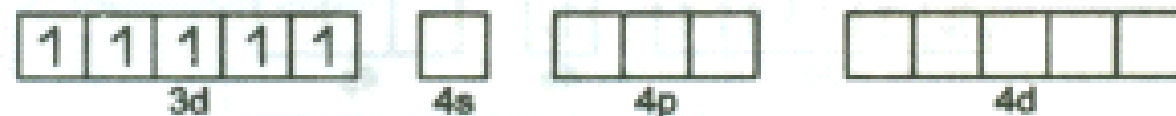
(Here oxidation number of Fe is x and H_2O is zero)

Now Fe is in (+3) O.S

Fe is in G.S.

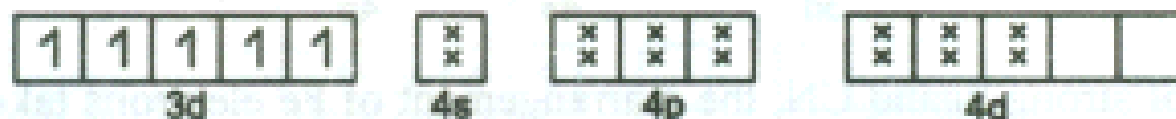


Fe is in (+3)O.S



Since H_2O is weak ligand, therefore the rearrangement of Fe electrons does not take place.

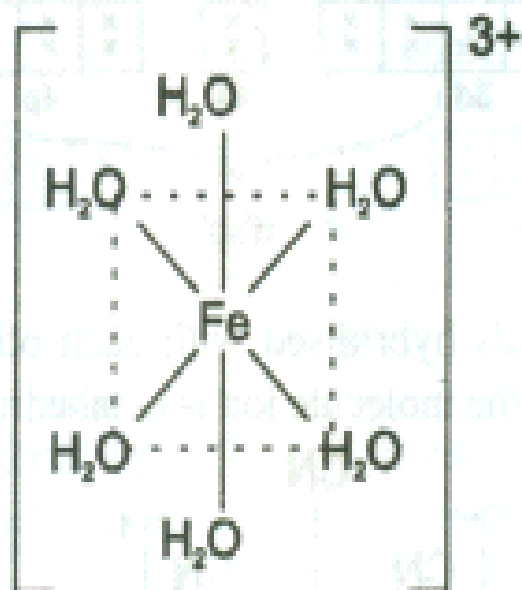
After hybridisation on filling the electrons of H_2O in empty orbitals of Fe metal



paramagnetic

sp^3d^2

Only s , three p and two d orbitals hybridised with each other to form $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, therefore hybridisation is sp^3d^2 and the shape of the molecule is octahedral.



paramagnetic

There is presence of unpaired electron in Fe metal orbital, the magnetic behaviour is paramagnetic.

4. $[\text{Ni}(\text{CN})_4]^{2-}$

Ni = 28

The atomic number of Ni is 28

Atomic configuration of Ni, $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$

Oxidation state of Ni in $[\text{Ni}(\text{CN})_4]^{2-}$ is

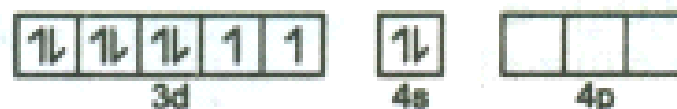
$$x + 4(-1) = -2$$

$$x = +2$$

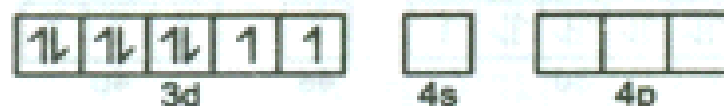
(Here oxidation number of Ni is x and (N is (-1)))

Now Ni is in $(+2)$ O.S

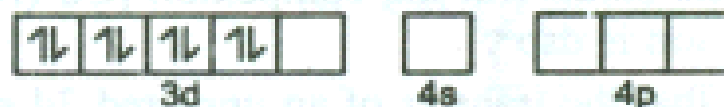
Ni is in G.S.



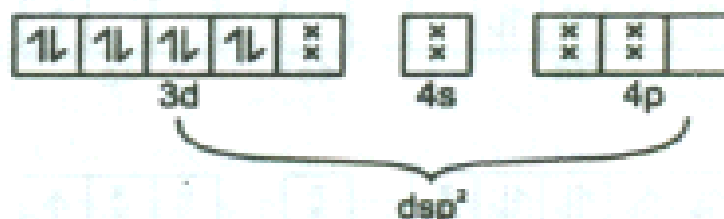
Ni is in $(+2)$ O.S



Due to influence of strong ligand CN, the rearrangement of Ni electrons take place.

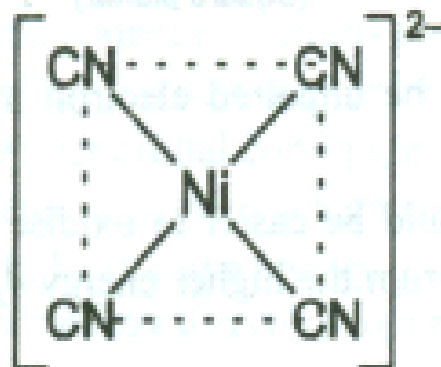


After hybridisation on filling the electrons of CN in empty orbitals of Fe metal



diamagnetic

Only d , one s and two p orbitals hybridised each other to form $[\text{Ni}(\text{CN})_4]^{2-}$, therefore hybridisation is dsp^2 and the shape of the complex is square planar.



diamagnetic

There is no of unpaired electron in Ni metal orbital, the magnetic behaviour is diamagnetic.

Short Comings of Valence Bond Theory

(i) Consider the complex



The atomic no of Cu is 29

Atomic configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

Oxidation state of Cu in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is

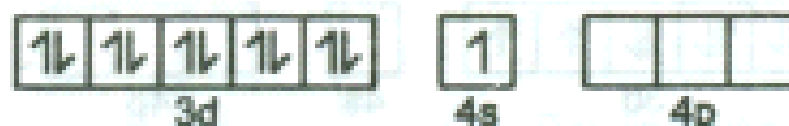
$$x + 4(0) = +2$$

$$x = +2$$

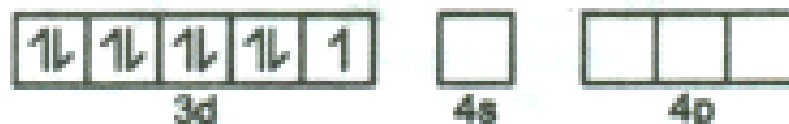
(Here oxidation number of Cu is x and NH_3 is zero)

Now Cu is in (+2) O.S

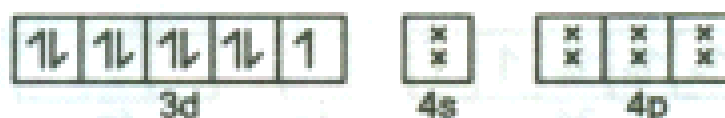
Cu is in G.S.



Cu is in (+2)O.S

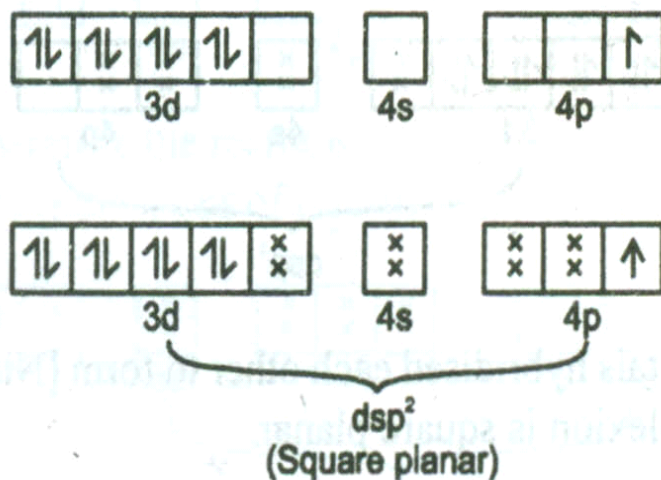


After hybridisation on filling the electrons of NH_3 in empty orbitals of Cu metal.



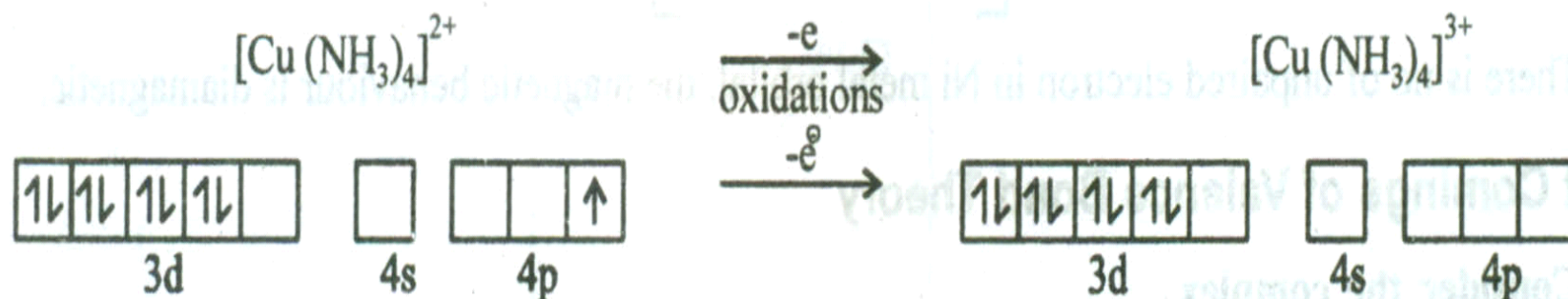
Only s , three p orbitals hybridised each other to form $[\text{Cu}(\text{NH}_3)_4]^{2+}$, therefore hybridisation is sp^3 and the shape of the complex ion tetrahedral. But the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ exists in square planar structure and therefore hybridisation is dsp^2 .

The valence bond theory suggests that the transfer of an unpaired $3d$ electron of $\text{Cu}(\text{II})$ to the higher energy $4p_z$ orbital is essential to bring about dsp^2 hybridisation.



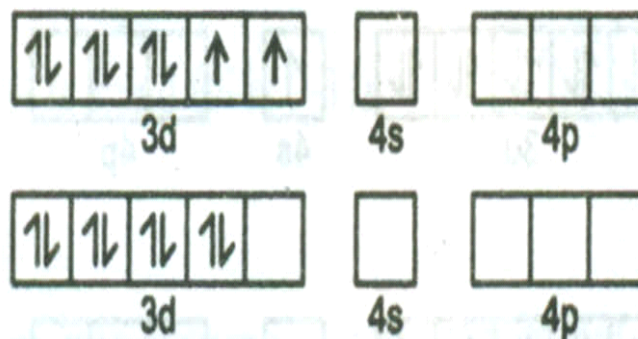
However, the ESR spectra reveal that the unpaired electron in such complexes is not permanently located in the $4p_z$ orbital of Cu(II).

Valence bond theory suggest that it would be easier to oxidise Cu(II) to Cu(III) in its square planar structure since the removal of electron from the higher energy $4p_z$ orbital would be quite easy.

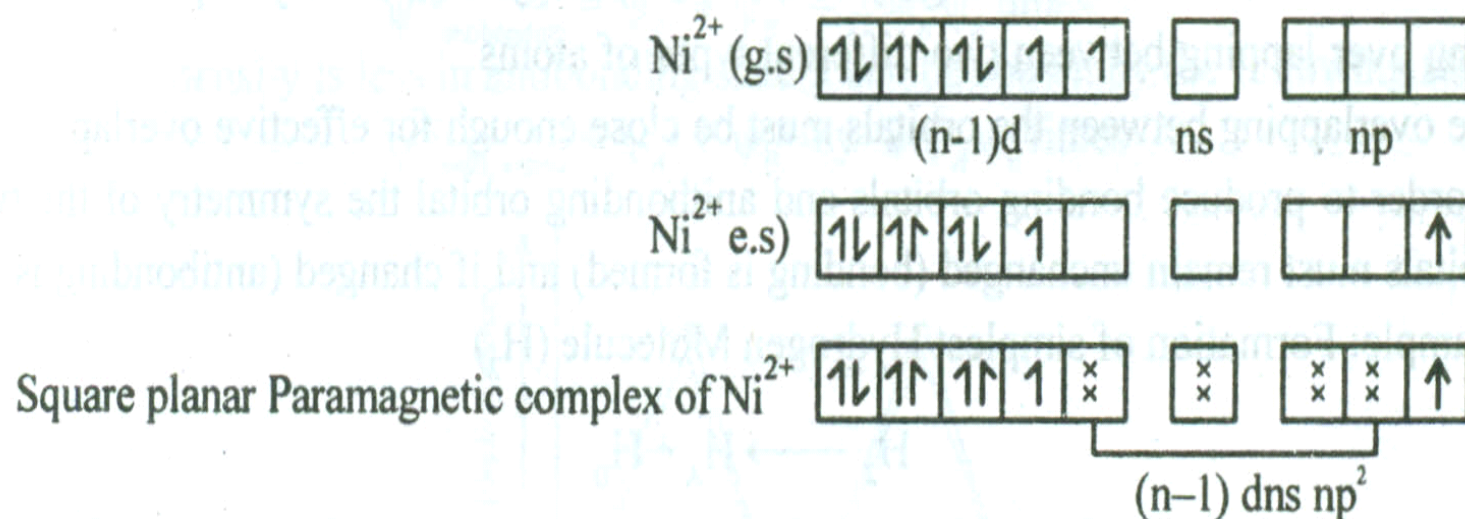


But it is contrary to facts for instance the oxidation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to $[\text{Cu}(\text{NH}_3)_4]^{3+}$ does not occur at all.

- (ii) The valence bond does not explain satisfactorily why some complexes of a metal ion in a particular oxidation state are low spin (inner orbital), while some other are high spin (outer orbital) complex for eg. $[\text{Cu}(\text{NH}_3)_6]^{3+}$ and $[\text{CoF}_6]^{3-}$
- (iii) The geometry of a complex and its magnetic behaviour is some times quite misleading square planar complex Ni^{2+} should be diamagnetic as shown below.



This may lead to the hybridisation $(n-1)dsp^2$. Conclusion that all square planar complexes of Ni (ii) should be diamagnetic but actually it is not so. Some square planar complexes are paramagnetic.



Valence bond theory does make an attempt to explain this observation by postulating that in such complexes one of the unpaired $(n-1)d$ electrons of Ni^{2+} get transferred to the vacant $4p_z$ orbital to vacate the $(n-1)d$ orbital which is required for $(n-1)dsp^2$ hybridisation to form square planar complex. But it is difficult to explain why such excitation of electron of electrons occurs in one square planar complex but not in the other.