Valence bond theory:

From the Werner's theory, it is noted that octahedral stereochemistry is involved with coordination no. 6. For coordination no. '4' two types of stereochemistry is involved tetrahedral and square planar.

Features of VBT →

(1) The central metal atom of the co-ordination entity loses a requisite no. of e^- from the valence shell. In some cases, the metal atom doesn't loose electrons.

(2) The central metal atom makes available number of empty valence shell orbitals [(n-1)d, ns, np] which is equal to C.N.

(3) The empty or vacant orbitals hybridize to form a set of equivalent hybridized orbitals.

(4) The valence electrons of the central metal ion explains the magnetic behaviour of the co-ordination compound.

(5) The ligands possess at least one pair of electrons occupying a valence shell orbital (σ-orbital) of the donor atom of the ligand. This filled orbital overlap with the vacant hybridized orbital of the central metal ion to form L→M σ bond.

(6) The ligands possess vacant π-orbitals (π-acceptor ligands) then electrons of filled π-metal orbitals may be donated to ligand to form M→L π bonds.

Different types of geometry and hybridization of coordination entity

For coordination number '4', the possible geometry and hybridization are →

(i) Tetrahedral (sp^3)

(ii) Square planar (dsp^2)

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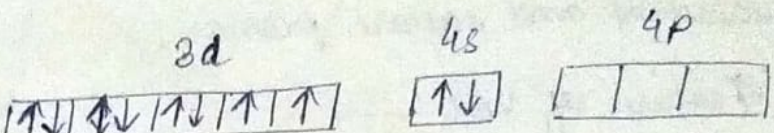
Illustration for coordination number (4).

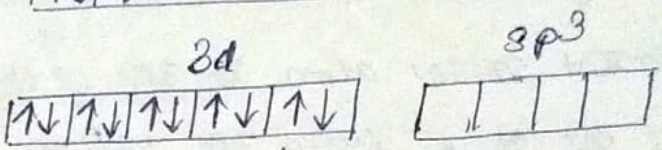
(i) formation of $[Ni(CO)_4]$

Ni has coordination number '4'. So, the species is tetrahedral. Therefore it must use vacant (sp^3) orbitals to form 6-bond with CO.

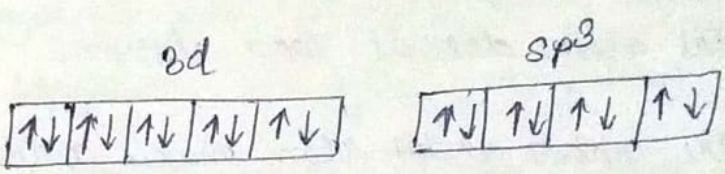
Valence shell of Ni



vacant sp^3 orbitals of Ni



Valence shell orbitals of Ni in $[Ni(CO)_4]$

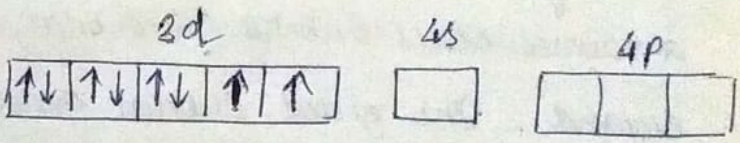


(ii) Square planar geometry and use of dsp^2 orbital.

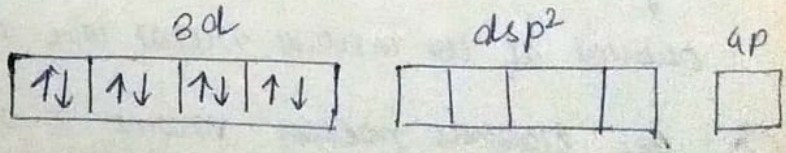
Formation of $[Ni(CN)_4]^{2-}$

Ni give up two electrons to form Ni^{2+} with C.N '4' here the coordination entity is square planar. So. Thus Ni^{2+} uses (dsp^2) hybrid orbitals to form bond with CN^-

Valence shell of Ni^{2+}



vacant dsp^2 orbital of Ni^{2+}



Valence shell orbitals of Ni in $[Ni(CN)_4]^{2-}$

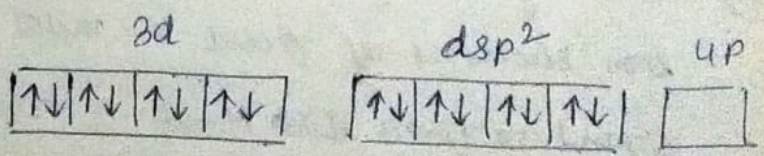


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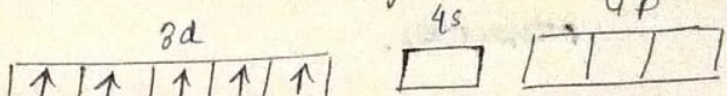
Illustration of coordination no. 6

The hybrid orbitals used by central metal atom or ion to form 6-bond with ligand is either d^2sp^3 or sp^3d^2.

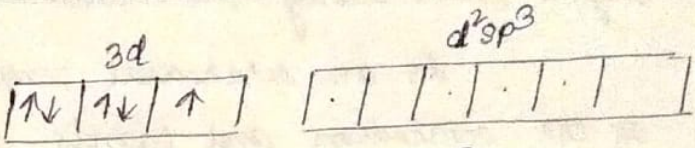
① Formation of $[Fe(CN)_6]^{3-}$

In this octahedral specie Fe^{3+} uses d^2sp^3 hybrid orbitals to form bonds with six CN^- ligands.

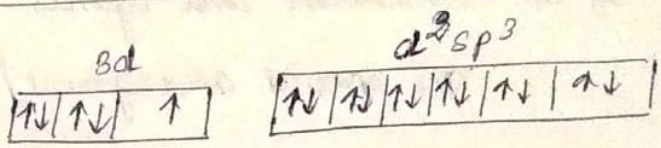
Valence shell orbital of Fe^{3+}



Vacant d^2sp^3 orbital of Fe^{3+}



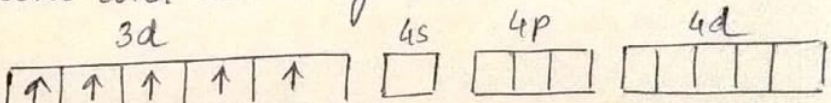
Valence shell orbitals of Fe^{3+} in $[Fe(CN)_6]^{3-}$



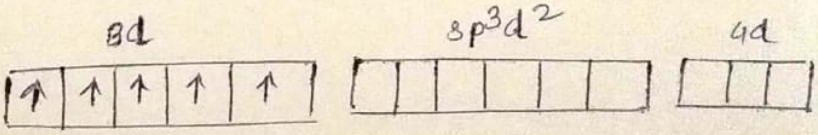
formation of $[FeF_6]^{3-}$

In an octahedral complex Fe^{3+} uses sp^3d^2 hybrid orbitals to form bond with six F^- ligands.

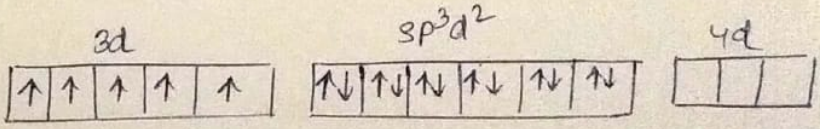
Valence shell orbital of Fe^{3+}



Vacant sp^3d^2 orbitals of Fe^{3+}



Orbital of Fe^{3+} in $[FeF_6]^{3-}$



Limitation of VBT

① This theory cannot explain the spectral properties of a complex which is related to the colour of the complex.

② The theory cannot explain the kinetic stability of a complex.

③ The theory cannot interpret the magnetic data quantitatively.

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