6. VALENCE BOND THEORY

Assumptions of Valence Theory

1. For the formation of a coordinate covalent bond, the central atom or ion in the complex provides a number of empty orbitals equal to its coordination number. For this purpose, appropriate ligand orbitals are required.

2. For the formation of strong bond between the metal and the ligand, the overlap of metal orbitals with ligand orbitals should be as effective as possible. For this purpose, the original atomic orbitals of the metal may undergo hybridization to form a new set of equivalent orbitals with definite directional properties.

3. Each ligand must contain at least one pair of electrons for the purpose of donation and forming a σ bond.

4. A coordinate covalent sigma bond is formed when a vacant orbital of the metal overlap with the filled orbital of the ligand. The coordinate covalent bond thus has a considerable amount of polarity due to the mode of formation.

5. The metal electrons which do not take part in the hybridization occupy the inner d orbitals. They are known as non-bonding metal electrons.

6. There is also a possibility of formation of a π bond in addition to a σ bond. This is possible when filled d orbitals of the metal can overlap with empty orbitals of the ligand. This kind of π bonding increases the strength of sigma bond and changes the charge distribution on both the metal and the ligand.

7. From the knowledge of the number of unpaired electrons in the complex thus formed, it is possible to predict the geometry and the magnetic properties of the complex and vice versa.

BONDING IN COORDINATE COMPLEXES

Tetrahedral complexes: formed by sp³ hybridization.

Example 1- [NiCl₄]²⁻
Electronic configuration of ⁴⁸Ni – 1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d⁸
Electronic configuration of Ni²⁺ – 1s², 2s², 2p⁶, 3s², 3p⁶, 4s⁰, 3d⁸
The observed magnetic moment of the complex is 2.95 BM. The calculated magnetic moment of the complex is 2.82 BM. The two values are close. This shows that the complex ion has two unpaired electrons and it is paramagnetic. The sp\(^3\) hybridization suggests tetrahedral geometry. In practice, the observed geometry of the complex is tetrahedral.

Example 2 - [MnCl\(_4\)]\(^2-\)

Electronic configuration of \(\text{Mn}^{2+}\) – 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 4s\(^0\), 3d\(^5\)

Electronic configuration of \[\text{MnCl}_4\]\(^2-\) – 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 4s\(^0\), 3d\(^5\)

The observed magnetic moment of the complex is 5.95 BM. The calculated magnetic moment of the complex is 5.92 BM. The two values are close. This shows that the complex ion has five unpaired electrons and it is paramagnetic. The sp\(^3\) hybridization suggests tetrahedral geometry. In practice, the observed geometry of the complex is tetrahedral.

**Square Planar Complexes: formed by dsp\(^2\) hybridization**

Example 1 - [Ni (CN)\(_4\)]\(^2-\)

Electronic configuration of \(\text{Ni}^{2+}\) – 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 4s\(^0\), 3d\(^8\)
6. VALENCE BOND THEORY

The unpaired electrons in the ground state of Ni$^{2+}$ ion, pair up in the excited state. The pairing energy is supplied by the formation of four strong bonds in the complex. Since all the electrons are paired, the [Ni (CN)$_4$]$^{2-}$ complex ion becomes diamagnetic. The observed & calculated magnetic moment of the complex is zero. The central metal ion undergoes dsp$^2$ hybridization and the complex ion takes square planar geometry.

**Example 2-** [Cu (NH$_3$)$_4$]$^{2+}$

Electronic configuration of 29Cu - 1s$^2$, 2s$^2$, 2p$^6$, 3s$^2$, 3p$^6$, 4s$^2$, 3d$^9$

Electronic configuration of Cu$^{2+}$ - 1s$^2$, 2s$^2$, 2p$^6$, 3s$^2$, 3p$^6$, 4s$^0$, 3d$^9$

This complex ion has a square planar geometry. It is paramagnetic and has magnetic moment 1.8 BM. This shows that the complex ion has one unpaired electrons and it is paramagnetic. The central metal ion undergoes dsp$^2$ hybridization and the complex ion takes square planar geometry.

The promotion of one electron from 3d to 4p orbital is not completely satisfactory. The 4p electron would be expected to be easily lost which means that the complex could be easily oxidized from Cu$^{2+}$ to Cu$^{3+}$. But this is not so.

If we place the unpaired electron in the 3d orbital, it would suggest sp$^3$ hybridization. That would suggest a tetrahedral geometry which is contrary to the observation.
The use of 4d orbital (outer orbital) to form sp²d hybridization is also not possible because the promotion energy would be too high and that would make the complex unstable. However, the complex is highly stable.

The failure to explain satisfactory explanation of the bonding in stable complexes such as [Cu (NH₃)₄]²⁺ is a major weakness of the VBT.

Octahedral Complexes-
These are formed by d²sp³ or sp³d² hybridization

1) d²sp³ hybridization: When two orbitals, (dₓ²−y²) and dᶻ² of (n-1) shell, one s-orbital of last shell n, take part in hybridization, it is known as d²sp³ hybridization.

Example 1- [Co (NH₃)₆]³⁺
Electronic configuration of 27Co – 1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d⁷
Electronic configuration of Co³⁺ – 1s², 2s², 2p⁶, 3s², 3p⁶, 4s⁰, 3d⁶

The four unpaired electrons in the ground state of Co³⁺ ion, pair up in the excited state. Thus two vacant d orbitals are created. Since all the electrons are paired, the [Co (NH₃)₆]³⁺ ion becomes diamagnetic. The observed & calculated magnetic moment of the complex is zero. The pairing energy is supplied by the formation of six strong bonds in the complex. The central metal ion undergoes d²sp³ hybridization and the complex ion takes octahedral geometry.

Example 2- [Fe (CN)₆]³⁻
Electronic configuration of 26Fe – 1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d⁶
Electronic configuration of Fe³⁺ – 1s², 2s², 2p⁶, 3s², 3p⁶, 4s⁰, 3d⁵
The five unpaired electrons in the ground state of Fe\(^{3+}\) ion, pair up in the excited state. Thus two vacant d orbitals are created. This leaves one unpaired electron in one d orbital. The [Fe (CN)\(_6\)]\(^{3-}\) ion becomes paramagnetic. The observed magnetic moment of the complex is 2.3 BM & calculated magnetic moment of the complex is 1.73 BM. The central metal ion undergoes d\(^2\)sp\(^3\) hybridization and the complex ion takes octahedral geometry.

ii) sp\(^3\)d\(^2\) hybridization: When one s orbital, three p orbital and two d orbitals, (d\(_x^2-y^2\)) and d\(_z^2\) of the same shell i.e. the last shell take part in hybridization, it is known as sp\(^3\)d\(^2\) hybridization.

The explanation of bonding for some octahedral complexes can be given in a similar way but central metal ion in these complexes undergoes sp\(^3\)d\(^2\) hybridization instead of d\(^2\)sp\(^3\) hybridization and keeps the same number of unpaired electron as in the free ion. The sp\(^3\)d\(^2\)-complex have the same geometry as that of d\(^2\)sp\(^3\) complex.

**Example 1-** [Fe F\(_6\)]\(^{3-}\)

Electronic configuration of Fe – 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 4s\(^0\), 3d\(^5\)

Electronic configuration of Fe\(^{3+}\) – 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 4s\(^0\), 3d\(^5\)

There are five unpaired electrons in the free Fe\(^{3+}\) ion so also five unpaired electrons in the [Fe F\(_6\)]\(^{3-}\) complex ion. The complex ion is found to be paramagnetic. The observed
magnetic moment suggests the presence of five unpaired electrons. The complex ion is octahedral in shape.

**Example 1- [Ni(NH₃)₆]²⁺**

Electronic configuration of ⁵⁸Ni – 1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d⁶

Electronic configuration of Ni²⁺ – 1s², 2s², 2p⁶, 3s², 3p⁶, 4s⁰, 3d⁸

There are two unpaired electrons in the free Ni²⁺ ion so also two unpaired electrons in the [Ni(NH₃)₆]²⁺ complex ion. The complex ion is found to be paramagnetic. The observed magnetic moment suggests the presence of two unpaired electrons. The complex ion is octahedral in shape.

**Inner and outer orbital complexes:**

Paling’s theory faces difficulties when the number of orbitals needed to accommodate the bonding electrons is too low. This can result from the occupancy of the orbitals by either paired or unpaired electrons from the metal ion. e.g. [Fe F₆]³⁻ and [Ni(NH₃)₆]²⁺ which have magnetic moment corresponding to five and two unpaired electrons respectively. In either of these cases, it is not possible to have d²sp³ hybridization of the central metal ion as shown below, there are only four orbitals (4s and 4p) of approximately same energy beyond the occupied orbital.
Huggins, in 1937, proposed that outer d orbital might be used in bond formation. However, at that time, it was generally considered that the 4d orbitals could not hybridize satisfactorily with 4s and 4p orbitals to give strong covalent octahedral bonds.

Craig showed that with highly electronegative ligands the use of 4d orbitals probably leads to stronger bonds than those formed by 4s & 4p orbitals alone.

In general, inner orbital octahedral complexes utilize (n-1)d^2, ns, np^3 orbitals and show d^2sp^3 hybridization and outer orbital octahedral complexes utilize ns, np^3,nd^2 orbitals and show sp^3d^2 hybridization, where n is the principal number of the outermost shell. The octahedral complexes like [Co (NH_3)_6]^{3+} which utilize (n-1)d, ns & np orbitals of the metal ion to show d^2sp^3 hybridization are called inner orbital complexes.

Whereas the octahedral complexes like [Ni(NH_3)_6]^{2+} which utilize ns, np & nd orbitals of the metal ion to show sp^3d^2 hybridization outer orbital complexes.

Inner orbital complexes are also called low spin or spin paired because in contain more number of unpaired electrons, while outer orbital complexes are called spin free or high spin.

**Electroneutrality principle:**

One of the objections raised to Pauling VBT of coordination compound was that there would be an accumulation of negative charge on the central metal atom or ion during the formation of a complex. The charge developed on the metal and the ligand due to the shift of the electron pair is called as formal charge. Thus in octahedral complexes, the formal charge on Fe in [Fe(H_2O)_6]^{3+} is −3, in [Fe(H_2O)_6]^{2+} is −4, in [Fe(CN)_6]^{4−} is −4. The formal charge on the central metal is obtained by subtracting the original charge on the metal from the total number of electron pairs shared between the metal and the ligands. for e.g. [Fe(H_2O)_6]^{2+}, the original charge on Fe is +2 while the charge due to the six electron pairs shared between Fe and H_2O is −6. Thus, the formal charge on the Fe would be (-6 + 2) = - 4 Pauling suggested that such a situation would not arise, due to two reasons -

1) Generally ligands are fairly electronegative hence the electrons will not be shared equally between the metal and the ligands thus inducing positive charge on the metal to balance the unfavorable formal charge and

2) The complex would be most stable when electronegativity of the ligand was such that the metal achieved essentially a neutral condition. This rule is known as electroneutrality principle.
Pauling electroneutrality principle states that “electrons are distributed in a molecule in such a way as to make the residual charge on each atom zero or very nearly zero except that hydrogen and the most electronegative metals can acquire partial positive charge and the most electronegative atoms can acquire partial negative charge.” The charge on the atom is decreased by (i) a change in the polarity or (ii) a change in the amount of ionic character of a bond.

This principle is applicable to complexes which are unstable because of the accumulation of the excessive negative charge on the metal. In such complexes bonds are partially ionic and partially covalent. We can illustrate the principle by taking an example of the complex ion Fe(H₂O)₆³⁺. If all the Fe-O bonds are 100% ionic, then entire charge 3⁺ would be located on the Fe atom. This implies that electrons are not shared and the electrons are not shared and the electrons of the ligands remain with oxygen atoms only. If all the Fe-O bonds are 100% covalent i.e. there is equal sharing of electrons between Fe and O atoms of ligands, the formal charge on Fe would be (-6 +3) = -3. when oxygen atom donates an electron pair it gets +1 formal charge and Fe atom gets –1 formal charge. Thus in 100% covalent bonding, each oxygen gets +1 formal charge and Fe would be left with (-6 +3) = -3 formal charge.

If the Fe – O bonds are 50% ionic and 50% covalent each oxygen would get +½ formal charge and Fe would get –½ formal charge per shared pair of electrons. Since Fe shares six electron pairs, it would get 6 x (-½) = -3 charge which would be cancelled by its
original charge +3. Thus the residual charge on Fe would be zero. However oxygen atom would be reluctant to bear a positive charge and therefore electrons of hydrogen atoms would be displaced towards oxygen atom. The net effect would be that each hydrogen atom would get \(+\frac{1}{4}\) formal charge. Thus the oxygen atoms become neutral. The +3 charge, which was distributed on oxygen atoms, would now share by 12 hydrogen atoms when the bonds are 50\% ionic. Thus the shift of electron pairs and charge distribution takes place in such a way that the formal charge \(-3\) on Fe is neutralized. This gives stability of the complex. This is shown below.

**Multiple bonding:**

According to VBT ligand must contain at least one lone pair of electrons for the purpose of donation and forming a \(\sigma\) bond. There are many ligands such as CO, RNC, PX\(_3\) (X- halogens), PR\(_3\), AsR\(_3\), SR\(_2\) etc. which are very poor electron donors and yet they forms many stable metallic complexes.

Pauling supposed that atoms of transition metals are capable of forming multiple bonds with electron accepting groups by making use of the electrons and orbitals of the shell below the valence shell. That is, in addition to sigma bond, a \(\pi\) bond may be formed between the metal and ligand. In this case, electrons are donated by the metal to the ligand to form the \(\pi\) bond. This back bonding in which the metal shares its own pair of electrons with the ligand, offset the accumulation of negative charge on the metal and strengthens the \(\sigma\) bond.

There are mainly two types of \(\pi\) bonding found in the complexes.

1) **Donation of electrons from metal d orbitals (t\(_{2g}\)) to empty p orbitals of the ligands.**

   This type of bonding is generally referred to as \(d\pi-p\pi\) bonding. It occurs when the ligand contains an atom from second row e.g. N in NO\(_2\), C in CO, or C in CN\(^-\).

2) **Donation of electrons from metal d orbitals (t\(_{2g}\)) to empty d orbitals of the ligands.**

   This type of bonding is generally referred to as \(d\pi-d\pi\) bonding. It occurs when the ligand contains an atom from third or later row e.g. P, S etc.

Ni-C bond distance in Ni(CO)\(_4\) is shorter than that expected for a single bond. This suggests that the bond has an appreciable amount of double bond character. The VB representation of the metal –carbon double bond requires that the carbon –oxygen bond be changed to double bond in order to vacate a p orbital for \(d\pi-p\pi\) bonding.

Let us consider a bonding between a metal like Ni, which has an available nonbonding pair of d electrons, and a ligand like PX\(_3\), which is a poor Lewis base. The filled
d orbital on the metal overlaps with one of the empty d orbital of phosphorus giving to dπ-dπ bonding.

Limitations of Valence Bond Theory:

Pauling VBT when applied to complexes has following drawbacks.

1. It gives only qualitative explanation regarding the structure, bonding and magnetic properties of complexes. It fails to give any quantitative explanation of these properties.
2. It can’t explain or interpret the spectra of the complexes.
3. It can’t explain why certain complexes are more liable than others.
4. It can’t account for or predict detailed magnetic properties.
5. In VBT it is assumed that all d orbitals are of equal energy. It does not consider the splitting of the d energy levels.
6. It does not account for the relative energies of different structures.
7. It fails to account for the observed geometries of certain complexes e.g. the tetragonal and distorted octahedral complexes.
8. It does not tell us why water and halide ions commonly form high spin complexes while cyanide ions form low spin complexes. e.g. why [NiCl_4]^{2-} is a high spin complex with a square planar geometry.
9. It does not give us any satisfactory reason for the formation of inner and outer orbital complexes.

In spite of these limitations, it can be said that VBT is simple and easy to apply and makes a good beginning to explain many things about the complexes.