CHAPTER I: PART A

INTRODUCTION
Ever since, Alfred Werner in 1893 put forward a theory which not only outlined a theoretical approach to explain the structure and behaviour of complex compounds, scientists found a new and fruitful field of investigation opened before them. At the present age the chemistry of coordination compounds is a very well established branch of the subject, which can be judged by proliferation of several monographs and wide variety of research papers appearing in established and new journals. The branch finds a place of pride among most of the modern branches of chemistry due to the important roles, the coordination compounds play in a large number of widely differing processes of biological and technological importance. Besides it is equally important to explain various complicated reactions and principles of fundamental chemistry.

Coordination compounds are primarily a consequence of the drastic changes of the metal ion properties in presence of appropriate ligand. Some ions and molecules which have independent existence and apparently saturated with respect to valence, have a tendency to combine in definite stoichiometric proportions to yield a new and more complex species, known as a complex compound was known to exist prior to
The complex compound so found has entirely different physical and chemical properties than the parent metal ion/molecule. In some, bonding appears to be essentially ionic, in others, it is clearly covalent. Although, the complex forming tendency is at a maximum among the transition metals and rare earths, the complexes play a significant role in the chemistry of all elements having electropositive character. Indeed, in a purely formal sense all or nearly all chemical compounds may be treated as coordination compounds. The point at which the formation becomes realistic and hence useful in practical sense is a matter subject to judgement to a degree, although there is surely a general agreement as to where the extreme lie.

A general definition of a complex or coordination compounds may be given as under -

A complex is formed when a central atom or ion (M) combines with one or more ligands (L)(L') etc., to form a species of the type, ML, ML', ML'', etc. In an attempt to make this definition more meaningful, some practical qualification are ought to be added:

i. that under chemically significant circumstances the central atom and the ion should be capable of existence, and

ii. that under such chemically significant condition the reaction involved in the formation of complex compound
from the central atom or ion and the ligand actually occurs.

The ligand may be defined as an atom, ion or molecule capable of functioning as the donor partner in one or more coordinate bonds. There may be cases for e.g., among the metal carbonyls where the partner we called the ligand, normally (Co) does approximately as much accepting as donating, but in general this definition will serve our purpose.

Attempts have been made by a large number of scientists for a theoretical interpretation of the data on the complex species. They contributed to the idea of some favourable factors which are observed in transition metals and rare earths, which are responsible for the greater tendency of forming complex compounds. The responsible factors are small cation size, comparatively large nuclear or ionic charges and appropriate electronic configuration. The addition of electrons to the \((n-1)d^{th}\) and \((n-2)f^{th}\) orbitals of transition metals and rare earths respectively goes on without any noticeable effect on the outermost \(n^{th}\), s and p orbitals. But, such filling, however, confers some characteristic properties like coordination number, magnetic properties, ability to form complexes etc. on such elements. The colour of the ions may be attributed to such fillings.

Alfred Werner, contributed a revolutionary paper\(^1\), which
not only outline theoretical approach to the structure and properties of complex compounds but also opened a new field of investigations. The award of Nobel prize in chemistry in 1913 was a fitting recognition of his accomplishment. The fundamental postulate of Werner’s coordination theory is best stated in his own words.  

“Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases the power of participating further in the contraction of the complex molecules with the formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact, that besides the affinity bonds designated as principle valencies, still other bonds on the atoms called auxiliary valencies may be called into action.”

Sidwick and Lowry independently made an electronic extension of Werner’s theory. They proposed an argument that the principle valency of Werner are involved, when electron transfer occurs, and the auxiliary valencies when the electron pair sharing takes place. They also noted that a majority of groups that coordinate to metal ions have molecular structures. For atoms with one or more non-bonded electron pairs, it was suggested that utilization of auxiliary valencies requires donation of electron pair from the coordinating species to the metal ion in question, with the formation of coordinate,
covalent, semipolar or dative bonds. The idea of shared pairs of electron in a coordinate bond leaves a question in mind as to the nature and necessary degree of such shairing. In many cases, the donor and acceptor are bound in such a way that the reaction of formation is not reversible to any detectable degree. Sidwick further suggested that the complex molecule is a group of covalently linked atoms, but some bonds may be formed by the shairing of electrons belonging to each of the linked atoms and the others may involve the electron belonging to one of the two linked atoms. A much similar but not satisfactory is that, a complex is one in which an atom has a covalence greater than its valence.10

Werner's view of secondary valency was supported by G. N. Lewis11 on the basis of his theory of valency. According to him the bond between the central ion and each of the attached groups involve a pair of electrons and is represented as a coordinate or dative bond. He also suggested that the shairing of an electron pair between two atoms is responsible for system involving them.

P. Ray12 classified complex compounds into two categories "Penetration complexes" and "Associated complexes". His observ-
vations were based on the magnetic studies of a number of complexes which was very well supported by Pauling's13 theory of quantum mechanics of coordination compounds.
Modern approaches involve the valence bond, crystal field and molecular orbital approximations. These approaches apply, most specifically to complexes of transition metals. In general, these approximations are based on magnetic, spectroscopic and structural data.

Valence Bond Theory:

L. Pauling\textsuperscript{13,14} in 1931, was the first to extend the V.B. approach to coordination compounds. The fundamental basis of this theory are the concepts of orbital hybridization, double bonding between metal and ligand and relationship of observed magnetic properties with the bond type. It has been pointed out that linear combination of hydrogen like wave functions, that are not geometrically equivalent may give sets of hybrid orbitals that are equivalent and geometrically oriented. The $s_p$ (linear), $s^3p$ (tetrahedral), $d^2s^2$ (square planar), $d^3p^3$ (trigonal bipyramidal) and $d^3sp^3$ (octahedral) are the most important hybrids for complex species, which result from presumed rearrangement to make orbital sub level to electrons provided by the ligand, although on occasions, such rearrangement may be unnecessary. It is a simple theory and widely utilized, but has been criticized due to lack of quantitative interpretation.

Crystal Field Approximation:

Since 1951, a radical revision of ideas concerning the
nature of bonding in complexes has come about by the application of the ideas of crystal or ligand field theory to chemical problems. Bethe\textsuperscript{15} and Van Vleck\textsuperscript{16} were the first to introduce this theory, which mainly applied to ionic crystals, but Orgel\textsuperscript{17} has been largely responsible for developing its general chemical aspects.

According to this theory, complex is regarded as an agglomeration of a central ion surrounded by other ions or molecules with electrical dipoles. The electric field of the central ion will affect the surrounding ligands, whilst the combined field of the ligand will influence the electrons of the central ion. Effect of the ligands is particularly marked on the d-electrons which play such a large part in complex formation by transition elements. The influence of the ligands depend on the nature, particularly on the strength of their electrical field, and on their geometrical positions in the complex.

A limited treatment of the problems, concerning the bonding between the central ion and the ligand is regarded as purely ionic so that the forces involved can be limited to electrostatic forces, is generally referred to as crystal field theory. This theory is basically concerned with the effect of the different arrangements of the surrounding ligands on the energy of the d-orbitals, and the sub-division of the orbitals into two groups, $t_{2g}$ and $e_g$. Under the influence of surrounding
ligand, d-orbitals are not energetically equal or in other words the degeneracy is resolved or split.

Negatively charged ions or molecules to be considered as ligand in complex have such a dipole that the negative end is closest to the central ion. Electrostatic field exerted by such ligands tend to repel the electrons (particularly the outer d-electrons), of the central ion and raises the energy level of the d-orbitals in the central ion. The ligand field depends on whether the ligands are arranged in an octahedral, tetrahedral or square planar way around the central ion. This effect of resolving on splitting the degeneracy of d-orbitals is known as crystal field splitting.\textsuperscript{18}

**Molecular Orbital Theory**

Molecular orbital theory was successfully applied to the metal complexes by J.H. Van Vleck\textsuperscript{16}. He pointed out that both the valence bond and crystal field theories are relatively simplified approaches to this more general approximation. Subsequent development of this theory for a detailed and comprehensive treatment to the problem of metal complexes was done by a few other scientists.\textsuperscript{19-24} The molecular orbital approximation in its simplest form, assumes the overlap of atomic orbitals as permitted by the symmetry and to the extent allowed by spatial orientation. Molecular orbitals based upon linear combination of these atomic orbitals result. Possible and
impossible overlap can be determined mathematically by the application of group theory. Molecular orbital approximations are better in accord with experimentally determined or measured properties than the other bonding approximation. Inclusion of \( \pi \) bonding is a major contribution by the molecular orbital approach.
Infrared Spectroscopy:

The excitation of molecular vibrations and rotations gives rise to absorption bands in the infrared regions of the spectrum. The spectra themselves are determined by the arrangement of atoms in space—their masses, bond lengths and angles—and by the forces between the atoms. When a ligand is coordinated, at least one additional atom—the atom to which the ligand coordinates—is introduced into the ligand’s vibrating system and bond lengths and angles, and interatomic forces within the ligand would be expected to alter slightly. This indicates that the infrared spectrum of a coordinated ligand will be different from that of the free ligand, and it should be possible to correlate the changes in spectra with the changes in geometry. In this way information about the structure of the complex may be obtained.

The differences between the spectra of free ligand and complex fall into three categories:

1. Band positions may change.
2. Relative band intensities may change. New, often weak bands appear.
3. Single peaks in the free ligand may split into several, closely spaced, bands in complex.

Interpretation of spectrum is carried out by comparing a
spectrum with that of a compound in which the ligand is coordi-
nated in a known way keeping mainly three points in mind:—

a. **Changes in band position**: Vibrational bands associated
with the stretching of bands involving the coordinated atoms
usually move to longer wavelength (lower energy) on coordination.

b. **Altered relative band intensities**: Appearance of new bands
in the spectrum may originate in several ways. New chemical
bonds formed as a result of coordination, from which corres-
ponding vibrations are to be expected. Coordination usually
reduces the effective symmetry of the ligand and so alters
the vibrational selection rules. As a consequence vibrations
which were infrared inactive in the isolated ligand may become
active in the coordinated ligand.

c. **Band splittings**: Just as a lowered symmetry on coordination
may cause the appearance of new bands, so it may cause the
splitting of bands, which are degenerate in the isolated
ligand.

**Electron Absorption Spectroscopy**

The energy required for the formation of an electron from
one orbital to another or, more precisely, the excitation of
a molecule from its electronic ground state to an electronic
excited state, corresponds to absorption of light in the near
infrared, visible or ultraviolet regions of the spectrum. For transition metal complexes the absorption bands in the first two of these regions are relatively weak and are associated with transition largely localized on the metal atom.

This change in the electronic structure also affects the vibrational, and possibly the rotational motions. Electronic transitions are considerably more rapid than the vibration of the molecule. Therefore, the distances between the atomic nuclei in the molecule are still unchanged in the first unit of time after an electronic transition. Due to this difference in the distance of nuclei of the excited molecule will be either "compressed" or "stretched" and therefore in a different vibrational mode than in the ground state. The adjustment of the nuclear distances corresponding to the excited state will give rise to further changes in the spectrum. The various conceivable transitions do not occur with equal probability. Some transitions have high extinction co-efficients, while other have low values. It is possible to predict very approximately the intensities of electronic absorption bands by a consideration of three theoretical rules called selection rules.27 There exists a number of different possible origins for the electronic absorption spectra of complexes. These are:

a. spectra associated principally with the ligand;
b. spectra involving electronic transitions between the
metal and the ligands; charge-transfer spectra;

c. spectra associated principally with the metal; influenced by the presence of the ligands, d-d spectra;

d. spectra associated with the counter-ion.

Magnetic Measurements:

When an atom or molecule is placed in a magnetic field any spin degeneracy may be removed. So, a level which is orbitally non-degenerate but which is a spin doublet may be split. If there is orbital degeneracy this too may be removed by the magnetic field. The splitting produced are very small, and are, for the vast majority of cases, proportional to the magnetic field. Because the splitting are so small, any particular atom or molecule may be in any one of several closely spaced states.

Closed shells of electrons have neither spin nor orbital degeneracy and are represented by a single wave function. A magnetic field, therefore, produces no splitting. It does, however, distort the electron clouds slightly in a manner akin to that predicted by Lenz's law in classical thermodynamics. That is, effectively, a small current is produced, the magnetic effect of which opposes the applied magnetic field. Because there is no resistive damping, the current remains until the magnetic field is removed. Molecules with closed shells
are therefore repelled by a magnetic field and are said to exhibit \textit{diamagnetism} or to be \textit{diamagnetic}. Molecules with unpaired electrons are attracted into a magnetic field and are said to exhibit \textit{paramagnetism} or to be \textit{paramagnetic}. For any transition metal ion which has both closed shells and unpaired electrons the two effects are opposed. All that can be measured is their resultant.

Magnetic susceptibilities were calculated by the formula:

\[ \chi_H = \frac{\chi_S \cdot W}{\Delta W} \]  \hspace{1cm} \text{\textit{1}}

where \( W \) is the weight of standard substance \( \Delta W \) is the increase in weight in magnetic field in miligram of the standard substance; \( \chi_S \) is the gram susceptibility of standard substance.

From the expression (1), gram susceptibility of the sample can be calculated by the formula:

\[ \chi_g = \chi_H \cdot \frac{\Delta W'}{W'} \]  \hspace{1cm} \text{\textit{2}}

where \( W' \) is the weight of sample, \( \Delta W' \) is the increase in weight in magnetic field in miligram of the sample substance; \( \chi_g \) is the gram susceptibility of the sample substance.

For chemical purpose it is most convenient to deal with molar susceptibilities.

\[ \chi_M = \chi_g \cdot M \]  \hspace{1cm} \text{\textit{3}}
where \( M \) is the molecular weight of the sample substance and \( \chi_M \) is the molar susceptibility of the sample substance.

To obtain the exact value of the paramagnetic susceptibility, and from this the effective magnetic moment (\( \mu_{\text{eff}} \)), the value of the diamagnetic susceptibility must be subtracted from the susceptibility calculated from the observed results. In the case of complexes having large organic ligands, which have small paramagnetic susceptibility, the diamagnetic susceptibility of the ligand is expediently determined experimentally, and this value is used for the correction purposes.

\[
\chi_A = \chi_M - \text{(- DMC)}
\]  

...(4)

where \( \chi_A \) is the atomic susceptibility of metal ion and DMC is the diamagnetic correction. From the paramagnetic susceptibility (\( \chi_A \)) so obtained, the effective magnetic moment (\( \mu_{\text{eff}} \)) is calculated from the following formula:

\[
\mu_{\text{eff}} = 2.84 \sqrt{\chi_A T}
\]

where \( T \) is the absolute temperature, \( \chi_A \) is the atomic susceptibility corrected for diamagnetic effects and \( \mu_{\text{eff}} \) is the magnetic moment of the substance in units of Bohr magnetons.

Amperometry — Ilkovic equation\(^{28}\) showed the simple relationship between the concentration of a substance and its diffusion current. This has helped in developing a highly sensitive
and convenient analytical technique called Amperometry or amperometric titrations. The principle of this technique is that if some of the electro-active material is removed by interaction with a reagent, the diffusion current will decrease. In amperometry potential applied across the indicator electrode and reference electrode is kept constant, at the plateau potential value of either of the titrate or titrant and the current passing through the cell is measured and plotted against the volume of reagent added.

In actual practice, the polarographic behaviour (current-voltage curves) of the reagent and the substance being titrated are obtained in a suitable supporting electrolyte. The potential is then fixed at the plateau value of the current-voltage curve of either of the reagent or the substance being titrated. A multiflex galvanometer is used to measure the current due to titrate at this potential. The reagent is then added drop by drop and the current at each addition is noted. The observed current is then plotted against the volume of reagent (titrant) added, to get current-volume curves. Owing to change in volume of the solution during the titration, an amperometric titration curve, must be a plot of \( i(V+V/V) \) against volume of reagent added, the factor \( (V+V/V) \) serves as a correction for dilution by reagent\(^{29,30}\). Some salient features of amperometric titration technique are described below:

1. The range and sensitivity are higher than potentiometric
and conductometric titrations, concentration from $1 \times 10^{-2}$ to $1 \times 10^{-4}$ mol dm$^{-3}$ and even in favourable cases $1 \times 10^{-6}$ mol dm$^{-3}$ can be measured.

2. Titration can be usually carried out rapidly since the end point is found graphically, a few current measurements at constant applied voltage before and after the end point suffice.

3. Amperometric titrations are very accurate and accuracy is higher than in polarography. Moreover, results of titrations are independent of capillary characteristics.

4. In cases, where the potentiometric or visual indicator method fails, this titration can be carried out. Amperometric titration is one of the few generally applicable procedure to the precipitation reactions.

5. It is immaterial whether the reaction which occurs during titration is, reversible, quasi-reversible or irreversible.
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