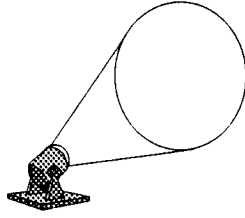


# CHAPTER-I



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## INTRODUCTION

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The transition or d block elements have intermediate properties between those of the s and p block elements and their penultimate shell is being expanded by the addition of d electrons.

Lanthanides, also known as 4-f block elements consist of fourteen members from La<sub>57</sub> to Lu<sub>71</sub> where the antepenultimate 4-f orbital is filled up. They have general electronic configuration [Xe] 4f<sup>1-14</sup> 5d<sup>1</sup> 6s<sup>2</sup>. These elements are characterized by lanthanide contraction, high electropositivity with M<sup>3+</sup>/M potentials varying from -2.25 V (Lu) to -2.52 V (La) and an aqueous chemistry of +3 ions.

Due to the presence of (n-1) d and 4f electrons and their transition to different energy levels they exhibit a number of physico chemical properties, such as magnetic, spectral, optical etc. These properties are used to increase the conductivity, magnetic susceptibility and optical properties of concerned materials. Lanthanides are used for the formation of bimetallic alloy film on some transition metals for example Sm-Ru. Bimetallic alloy films on Ru surface are formed by vapour deposition and annealing. The growth and surface chemistry of thin alloy film is a subject of great interest from the point of view of their basic scientific understanding and applications in areas such as adsorption and catalysis, hydrogen storage and surface magnetism.

The selection of the subject matter for this work has been guided not only by author's interest but also by the view that in a review of this nature, comprehensive treatment of a few topics is better than a limited treatment of many.

Few areas in the chemistry of rare earth elements have expanded as rapidly as that of co-ordination chemistry.

The ability of certain ions and molecules, which have independent existence and apparently saturated with respect to valency, are combined in stoichiometric proportions to yield a new and more complex species known as co-ordination compounds.

A large number of workers have attempted the studies and theoretical interpretation of the data on the complex species. They observed that the ability to form complex compounds is maximum among the transition metals and rare earths. This is possible in view of such favourable factors such as small cation size, comparatively large nuclear or ionic charge and appropriate electronic configuration. The addition of electrons to the  $(n-1) d^{\text{th}}$  and  $(n-2) f^{\text{th}}$  orbitals of transition metals and rare earths, respectively, goes on without any noticeable effect on the outermost  $n^{\text{th}}$  S and P orbitals but such filling however confers some characteristic properties like co-ordination number, magnetic and properties, ability to form complexes by such elements. Colour of their ions is also attributed to such fillings.

Alfred Werner<sup>1,2</sup> in 1893 contributed a revolutionary paper which not only outlined a theoretical approach to structure and properties of complex compounds but also opened a new and fruitful field of investigation. The fundamental postulates in Werner's coordination theory is best stated in his own words.

Even when to judge by the valence number, the combining power of certain atom is exhausted, they still possess, in most cases, the power of participating further in the construction 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 principal valencies, still other bonds on the atoms called auxiliary valencies may be called in to action.

The award of Nobel prize in chemistry, in 1913, was a fitting recognition of his accomplishment.

Sidwick<sup>3</sup> and Lowry<sup>4</sup> independently suggested that the principal valencies of Werner are involved, when electron transfer occurs and the auxiliary valencies when electron pair sharing takes place.

The inadequacies of the simple Sidwick extension of Werner's theory of bonding are emphasised by its inability to account even qualitatively for many of the observed properties of complex species.

Modern approaches involved the valence bond, crystal field and molecular orbital approximation. These approaches apply most

specifically to complexes of the d transition metals. In general they are based upon magnetic, spectroscopic and structural data.

### **Theories of Coordination Compounds**

#### **Valence bond theory :**

Valence bond theory was first extended to co-ordination compounds by L. Pauling<sup>5</sup> in 1931. The fundamental basis of this theory is the concept of orbital hybridisation, double bonding between metal and ligand and relationship of observed magnetic properties of the bond type.

This theory is simple but it has been criticised due to lack of quantitative interpretation.

#### **Crystal field theory :**

H. Bethe<sup>6</sup> and J.H. Van<sup>7</sup> Vleck put forward this theory, concerned with the electrostatic effects of a surrounding array of anions or electric dipoles on the properties of a central cation in a crystalline solid. It is concerned with electrostatic interaction between surrounding ligands, treated as dipole charges, and electrons in d orbitals of a central metal ion. All interactions in this approximation are completely electrostatic.

#### **Molecular orbital theory :**

Molecular orbital theory<sup>8,9</sup> in its simpler form assumes the overlapping of atomic orbitals as permitted by the symmetry and to the

extent allowed by spatial orientation. Molecular orbital theory is based upon linear combination of these atomic orbitals. Possible and impossible overlaps can be determined mathematically by the application of group theory. Molecular orbital approximations are better in accord with experimental determinations or measured properties, than the other bonding approximations. Inclusion of  $\pi$  bonding is a major contribution of the molecular orbital approach.

### **Physical methods used for the study of metal ligand complexation equilibria**

In the past, quite a good number of techniques have been employed by scientists for the study of metal : ligand complexation equilibria. Recently some electrochemical methods have attracted the attention of researchers for the said purpose. Among these electrochemical techniques polarography and its sister branches e.g. Amperometry, Biamperometry etc. have emerged as the powerful tools for such studies. The work has been supplemented by UV spectrophotometric studies.

In the present work the author has aimed to show the most important application of polarography i.e. in the field of co-ordination chemistry. The polarographic method of studying the dynamic process of electron transfer needs a complete understanding and evaluation of experimental data and a little bit more theoretical background than the static methods. This background is not

generally familiar to co-ordination chemists but without its knowledge, it is not possible to provide a correct interpretation of experimental data.

**Polarography** : Professor J. Heyrovsky<sup>10</sup> of Charles University in Prague discovered a new technique known as polarography in 1922 which may be defined as "A branch of electroanalytical chemistry that deals with the effect of the potential of an electrode in an electrolytic cell on the current that flows through it, where working electrode is a dropping mercury electrode".

The technique gained prominence only after 1935 when Ilkovic Kolthoff, Lingane<sup>11</sup> etc. provided the technique a mathematical background, so as to make it useful for analytical problems. A fitting recognition to its discoverer, Prof. Heyrovsky was given by awarding him Nobel prize in 1959.

**Basic Principles** : If a steadily increasing voltage is applied to a cell incorporating a standard calomel electrode as anode and minute mercury cathode, it is frequently possible to construct a reproducible current voltage curve<sup>12,13</sup>. The electrolyte is a dilute solution of a material (which must be electro active) under examination in a suitable medium containing an excess of an indifferent electrolyte, to carry the bulk of the current and raise the conductivity of the solution, thus ensuring that the material to be determined, if charged does not migrate to the dropping mercury electrode. From an

examination of the current voltage curve, information as to the nature and concentration of the material may be obtained [Fig. 1.1].

**Residual Current:** Mercury is matchless in being electrically uncharged when it is dropped freely into a solution containing a supporting electrolyte eg. potassium chloride. If a polarogram is recorded for a solution containing electroactive species a very small rise in current is observed before the decomposition potential. This increase in current is observed even when the purest air free solutions are used, hence it can not be due to the reduction of impurities. It must therefore be considered non faradic or condensor current, made appreciable by the continual charging of the fresh mercury drops to the applied potential. It is known that metals when submerged in an electrolyte are covered with an electrical double layer of negatively and positively charged ions. The capacity of the double layer and hence the charging current varies depending upon the potential which is imposed upon the metal.

In practice it is observed that supporting electrolyte contains traces of impurities so that small currents are superimposed upon condensor currents. It is customary to include all these in residual current. Ordinarily it is not possible to eliminate the residual current, hence it is necessary to account for it specially in polarographic study.

**Migration current :** The electroactive material can reach the micro-electrode by migration and diffusion processes. Heyrovsky showed



that the migration current can be practically eliminated if a supporting electrolyte is added to the solution in a concentration so large that its ions carry essentially all the current. In practice this means that concentration of the added electrolyte must be at least 100 folds to that of electroactive species under examination. If it is assumed that the conductance of each ion is approximately equal then it follows that maximum current will be transported by the ions of the base electrolyte. Under such conditions the electroactive material can reach the electrode only by diffusion. It must be emphasised that the supporting electrolyte must be composed of ions which are discharged at higher potential and which will not interfere or react chemically with the ions under investigation.

**Diffusion Current** : When an excess of supporting electrolyte is present in the solution the electrical force on the depolariser ion is nullified. This is because the ions of the supporting electrolyte carry practically all the current and the potential gradient is compressed to a region so very close to the electrode surface that it is no longer operative in attracting electroactive ions. Under these conditions the limiting current is almost solely a diffusion current.

The first solution to the problem of calculating the polarographic diffusion current was obtained by Ilkovic<sup>14</sup> and later on by Gillavery and Riedel. The solution can be written in the form

$$i_d = 607 n C D^{1/2} m^{2/3} t^{1/6} \text{ at } 25^\circ\text{C} \quad \dots\dots (1)$$

$i_d$  = Average diffusion current during the life of mercury drop

$n$  = The number of Faraday of electricity required per mole of electrode reduction or oxidation of electroactive species.

$C$  = Concentration in millimole per liter of electroactive substance

$D$  = The diffusion coefficient of the reducible or oxidisable substance expressed in  $\text{cm}^2 \text{s}^{-1}$

$m$  = The rate of flow of mercury from the dropping electrode expressed in  $\text{mg s}^{-1}$

$t$  = Drop time expressed in seconds.

When all other factors are constant we get  $i_d = KC$  i.e. the diffusion current is proportional to the concentration. Thus plot of  $i_d$  vs concentration of the substance should be straight line, if the wave is diffusion controlled. This forms the quantitative aspect of polarography.

Diffusion current is affected by the following factors :

1. The concentration of electroactive substance.
2. The capillary characteristics.
3. Temperature.
4. Solvent and supporting electrolyte.
5. pH of the test solution etc.

**Polarographic Maxima** : Polarographic maxima are frequently observed when polarogram is recorded with dme, and are recognised by the appearance of sharp peak or rounded hump at the top of the polarographic wave which is disadvantageous in all sort of polarographic studies.

**Maximum Suppressor** : To measure the true diffusion current, the maxima must be eliminated or suppressed. Fortunately, this can be done easily by the addition of a very small quantity of a surface active substance (Lyophilic or Lyophobic colloids) such as sodium methyl red, gelatin or triron X-100. Higher concentrations of suppressor may seriously effect  $i_d$  or the potential of the wave and should not be used without proper testing.

**Half Wave Potential** : In polarography each electroactive material is characterised by its half wave potential. This is the potential at the point of inflection of current voltage curve, at half the distance between the residual current and final limiting current plateau. It may also be defined as the potential on the polarographic wave where the current is equal to one-half of the total diffusion current. The half wave potential  $E_{1/2}$  is related to the standard oxidation potential by the equation :

$$E = E^\circ + \frac{RT}{nF} \log \frac{(OX)}{(Red)} \quad \dots\dots (2)$$

Where (OX) and (Red) are the diffusion coefficients of the appropriate oxidized and reduced species. This equation when solved for  $E_{1/2}$  value attains the following form :

$$E = E_{1/2} + \frac{0.0591}{n} \log \frac{i_d - i}{i} \quad \dots\dots (3)$$

This equation represents the potential as a function of current at any point on the polarographic wave and is some times termed as the equation of the polarographic wave.

The half wave potential is independent of the electrode characteristics and can therefore serve for the qualitative identification of an unknown substance.

**Limiting Current :** With the gradual increase in the applied potential, the current flowing through the polarographic cell increases upto a maximum value. Any further increase in the applied potential does not result in further increase in the current, i.e. the current acquires a limiting current plateau, because it represents the limiting or maximum rate at which the particular ionic species can be discharged under the given experiment conditions.

**Oxygen interference :** Oxygen dissolved in electrolytic solution is easily reduced on the dropping mercury electrode and produces two waves of approximately equal heights extending over a considerable voltage range. It is therefore necessary to remove any dissolved oxygen

from the electrolyte solution, whenever cathodic regions are being investigated in which oxygen interferes. This is easily done by passing an inert gas (usually nitrogen) through the test solutions for about fifteen minutes before recording the polarograms.

### **Polarographic study of metal complexes**

Polarography constitutes a powerful and versatile tool for the study of complexes in solution. When metal ion undergoes complexation with ligand its polarographic reduction wave is altered in two ways, firstly the  $E_{1/2}$  is shifted to more electropositive or electronegative value as compared to the metal ion. Secondly the diffusion current changes and usually becomes smaller.

Study of the stability of metal complexes polarographically involves the determination of shifts in halfwave potential or limiting current of metal ions, in presence of increasing amount of complexing agents<sup>15, 16</sup>.

Method for determination of stoichiometry and stability constant of metal complexes polarographically may be divided into three categories :

- (a) Formation of a single complex species
- (b) Formation of plural complex species (stepwise complex formation)
- (c) Mixed ligand complex formation of metal with two ligands.

**(a) Formation of a single complex species :** The treatment has been discovered by Lingane. In this step, for studying a reversibly reducible complex system, following equations are used to calculate the metal ligand ratio and stability constant of the complex

$$\frac{\Delta E_{1/2}}{\Delta \log C_x} = -p \frac{0.05915}{n} \quad \dots\dots (4)$$

and

$$(E_{1/2})_c - (E_{1/2})_s = \frac{0.0591}{n} \log k_c - \frac{0.05915}{n} p \log C_x \quad \dots\dots (5)$$

where,

$(E_{1/2})_c$  = Half wave potential of complex ion

$(E_{1/2})_s$  = Half wave potential of simple ion

$K_c$  = Dissociation constant of the complex

$C_x$  = Concentration of the ligand in moles

$n$  = Number of electrons involved in the electrode process

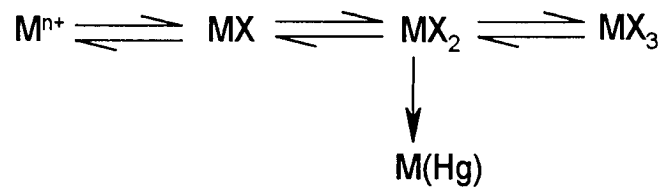
Thus a plot of  $E_{1/2}$  vs  $\log C_x$  should be linear with slope  $-p \frac{0.0591}{n}$

from which the co-ordination number  $p$  of the metal complex ( $MX_p$ ) may be calculated to give the stoichiometry of the complex.

## **(2) Formation of successive complex**

If the complexation takes place in steps, the Deford and Hume's<sup>17</sup> method may be successfully applied to evaluate the stability constant of each of the complex species formed, provided they are reversibly reduced at the indicator electrode.

To calculate the individual and overall stability constant for a reaction of the type



It is convenient to deal with the following equations

$$F_0(X) = \text{Antilog} \left[ \frac{0.4343nF}{RT} \Delta E_{1/2} + \log \frac{I_m}{I_c} \right] \quad \dots\dots (6)$$

$$\begin{aligned}
 F_0(X) = & \beta_0 + \beta_1[X] \frac{Y_m Y_X}{Y_{MX}} \\
 & + \beta_2 \frac{[X]^2 Y_m [Y_X]^2}{Y_{MX_2}} \\
 & + \beta_N \frac{[X]^N Y_m [Y_X]^N}{Y_{MX_N}} \quad \dots\dots (7)
 \end{aligned}$$

The initial term  $\beta_0$  is the stability constant of zero complex, which has a value of unity. When activity coefficient in above equation is dropped, we get

$$F_0[X] = 1 + \beta_1[X] + \beta_2[X]^2 + \dots\dots\dots \beta_N[X]^N \quad \dots\dots (8)$$

In order to determine  $\beta_1 \dots\dots\dots \beta_N$  Laden's<sup>18</sup> graphical extrapolation method has to be applied. From equation (8) it is clear that a plot of  $F_0[X]$  vs  $[X]$  will be a steeply rising curve. The curve will have a limiting value as  $[X]$  approach zero. Its intercept on the  $F_0[X]$  axis is the value of  $\beta_0$  which is equal to one. Thus the value of  $\beta_1$  may be obtained by equation -

$$F_1[X] = \frac{F_0[X]-1}{[X]} = \beta_1 + \beta_2[X] + \beta_N[X]^{N-1} \quad \text{..... (9)}$$

A plot of  $F_1[X]$  vs  $[X]$  will give slope of  $\beta_2$  and its intercept on  $F_1[X]$  axis will give  $\beta_1$ . The function  $F_2[X]$  may be similarly defined as

$$F_2[X] = \left[ \frac{F_1[X]-\beta_1}{[X]} \right] = \beta_2 + \beta_3[X] + \beta_N[X]^{N-2} \quad \text{..... (10)}$$

This procedure is continued and for penultimate complex  $MX_{N-1}$

$$F_{N-1}[X] = \left[ \frac{F_{N-2}[X]-\beta_{N-2}}{[X]} \right] \quad \text{..... (11)}$$

$$= \beta_{N-1} + \beta_N X \quad \text{.....}$$

and the final function  $F_N[X]$  will be independent of ligand concentration. Thus,

$$F_N[X] = \left[ \frac{F_{N-1}[X]-\beta_{N-1}}{[X]} \right] = \beta_N \quad \text{..... (12)}$$

On plotting  $F_N[X]$  vs  $[X]$ , a straight line parallel to X axis is obtained.

### (3) Formation of mixed ligand complex :

Schaap and Mc Masters<sup>19</sup> have developed a logical extension of the Deford and Humes method by applying the latter two cases where, metal ion forms complex with two ligand species simultaneously in solution.

If a complex reaction of the following type is considered





Where  $p$  and  $i$  are the stoichiometry numbers and  $X$ ,  $Y$  are two different ligand species. A new function  $F_{00}(X, Y)$  is introduced whose value is given in terms of measurable data for half wave potential shift by equation

$$F_{00}(XY) = \text{Antilog} \left[ \frac{0.4343nF}{RT} \Delta E_{1/2} + \log \frac{I_m}{I_c} \right] \quad (13)$$

For the simple case where a maximum of these bound ligands of type  $X$  and  $Y$  occurs,  $F_{00}$  functions lead to

$$\begin{aligned} F_{00}(X, Y) = & \left\{ \beta_{00} + \beta_{01}(Y) + \beta_{02}(Y^2) + \beta_{03}(Y^3) \right\} X^0 \\ & + \left\{ \beta_{10} + \beta_{11}(Y) + \beta_{12}(Y^2) \right\} [X] \\ & + \left\{ \beta_{20} + \beta_{21}(Y) \right\} [X]^2 \\ & + \left\{ \beta_{30} \right\} [X]^3 \quad \dots (14) \end{aligned}$$

Here  $Y$  is regarded as maintained constant while  $(X)$  is varied.

The  $\beta$ 's are single and mixed stability constants respectively.

For simplicity, above equation is expressed in the form :

$$F_{00}(X, Y) = A + B[X] + C[X]^2 + D[X]^3 \quad \dots (15)$$

Where  $A$ ,  $B$ ,  $C$  and  $D$  are constants, their values may be evaluated by graphical method.

On applying Laden's treatment to the  $F_{00}[X, Y]$  functions, we get:

$$F_{10} = \frac{F_{00} - A}{[X]} = \beta + C[X] \quad \dots (16)$$

and

$$F_{20} = \frac{F_{10} - B}{[X]} = C \quad \text{..... (17)}$$

From the calculated value of B, the value of  $\beta_{11}$ , mixed ligand formation constant, can be computed by equation.

$$B = \beta_{10} + \beta_{11}[Y] \quad \text{..... (18)}$$

In order to determine  $\beta_{21}$  and  $\beta_{12}$  it is necessary to determine the constant B at least at two different fixed concentrations of [Y]. Using this criteria the functions  $F_{ij}$  and hence the scheme for mixed ligand complex formation can be presented.

### **Amperometric titrations**

Amperometry<sup>20</sup> is a term used for a technique employed for the determination of the concentration of an electroactive substance from the current, which results from the reaction of the substance at an electrode.

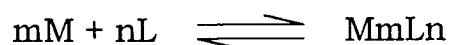
Amperometric titrations are used to follow the concentration change and thus to detect the equivalence point. During an amperometric titration the plateau potential of the depolariser is applied between the indicator electrode (DME) and reference electrode and is maintained constant. The current passing through the electrolytic cell is then determined on addition of each increment of titrant. For simple amperometry either the titrant or the species being titrated must exhibit polarographic activity.

On addition of some titrant, X, which reacts with the titre species 'M', the concentration of free M is reduced and as a consequence, the diffusion current to which it is proportional is also decreased. If both M and X are electroactive at the applied potential the diffusion current of M will decrease to the residual current line when it has fully reacted with X. As soon as X appears in excess its diffusion current will develop and will increase with continued titrant addition. Current *vs* titrant volume graphs will be V or L shaped, if both or only one of the species are electroactive respectively.

### **UV Spectrophotometry**

In many substances which are colourless, the electronic excitation may occur because of the absorption in UV region. Transitions are even influenced by the presence of neighbouring molecules and therefore UV Spectra, like the visible spectra, consists of one or more broad peaks. In the present case absorption studies were made on the observed complexation so as to establish the metal ligand equilibria. Systronics (India) UV visible spectrophotometer model-118 was used for absorption studies.

The nature of complex formed has been studied by following Job's<sup>21</sup> method of continuous variation. P. Job applied his method for the formation of complexes in solution for a reaction :



in which M = Metal ion and L is the ligand molecule. The ratio in which complex is formed, may be represented as  $\frac{m}{n} = \frac{(1-x)}{x}$ . Job suggested the following equations to calculate the stability constants :

for 1:1 complex  $m = n = 1$

$$K_s = \frac{(P-1)(1-2x)}{C[(P+1)(x-1)]^2} \quad \dots\dots (19)$$

and for 1:2 complex where  $m = 1, n = 2$

$$K_s = \frac{(P-1)^2(2-3x)}{C^2 P[(P+2)(x-2)]^3} \quad \dots\dots (20)$$

Where in the above equations

C = Molar concentration of metal ion

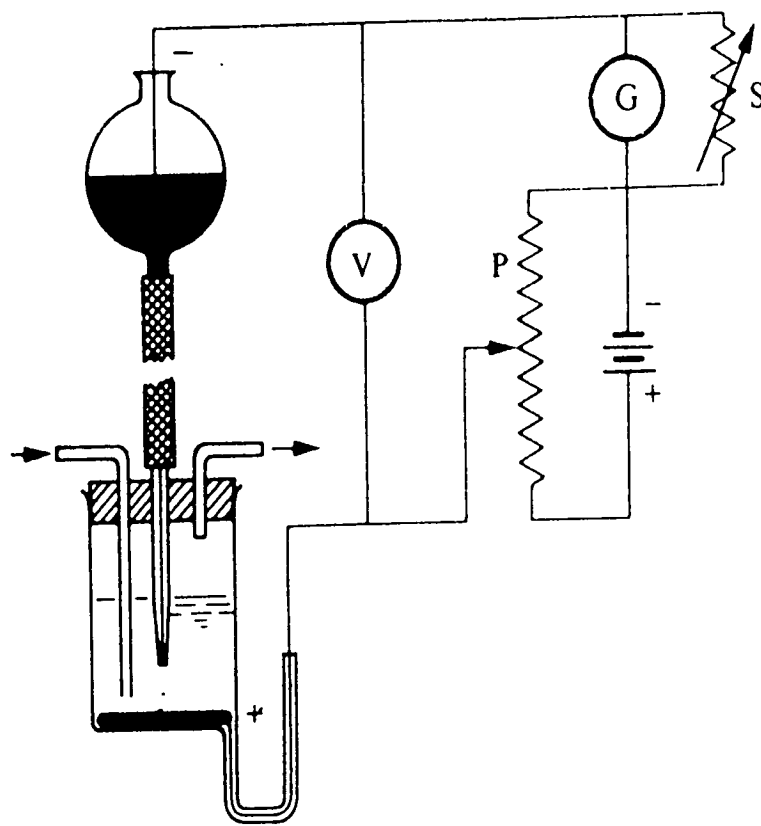
P = Ratio of molar concentration of ligand to that of metal

X = Volume fraction of ligand, where the maximum amount of complex is formed.

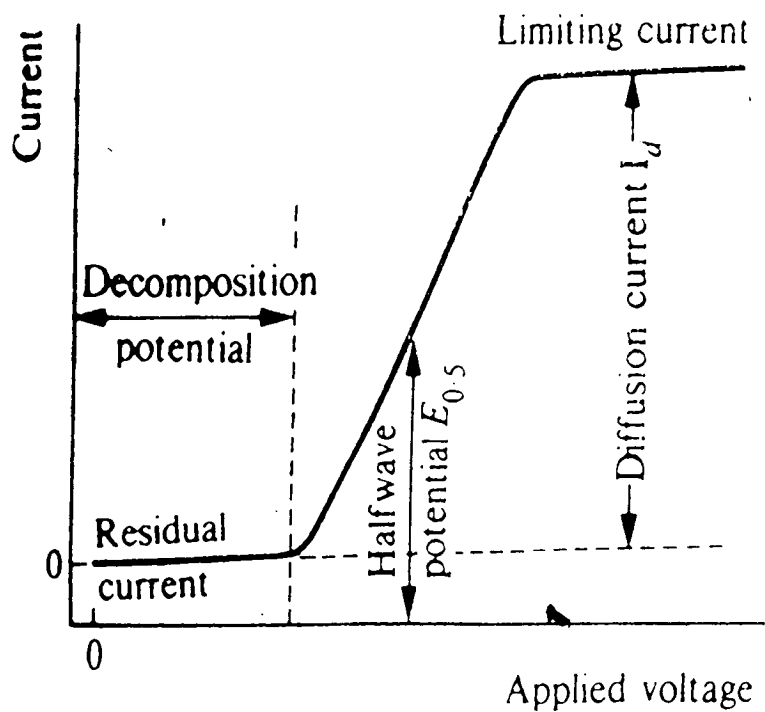
### **Aims and Applications of the present work**

Polarographic methods of analysis have made the study of binary and ternary complexes, easy. The technique being economic and convenient for the study of different type of reactions has proved its usefulness in research laboratories and academic institutions. A survey of literature reveals some special advantages of polarography<sup>22-41</sup>. Keeping this in mind the author has used the techniques systematically for the following :

- (1) Studies on some binary complexes of  $Zr^{4+}$ ,  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$  and  $Sm^{3+}$  involving single step and multiple step complexation reaction.
- (2) Studies on some mixed ligand complexes of  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$  and  $Sm^{3+}$ .
- (3) Amperometric titration of  $Zr^{4+}$ ,  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$  and  $Sm^{3+}$  with some azo dyes.
- (4) Spectral studies on metal ligand complexation involving ligands used for amperometric and complex formation equilibria in the present work, to establish the stoichiometric ratio of the complexes and to calculate their formation constants.



**Fig. 1.01 The basic apparatus for polarographic analysis**



**Fig. 1.02 The typical current - applied voltage curve (Polarogram)**

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