Chapter-2

GENERAL PRINCIPLES OF POLAROGRAPHY
Section(i): Theory and Application of Polarography

Voltammetry comprises a group of electro analytical methods in which information about the analyte is derived from the measurement of current as a function of applied potential obtained under conditions that encourage polarization of the indicator or working electrode. Generally, the working electrodes in Voltammetry are characterized by their small surface area [usually a few square millimeters] which enhances polarization. Such electrodes are generally referred to as micro electrodes.

At the outset, it is worthwhile pointing out the basic differences between Voltammetry and the two types of electrochemical methods viz: Coulometry and Potentiometry. Voltammetry is based upon the measurement of a current that develops in an electrochemical cell under conditions of complete concentration polarization. In contrast, in potentiometry the unknown potential of an electrode is measured against a reference electrode with known potential by balancing the potential difference between the two against a known but opposite voltage. During this balancing process every effort is made to avoid any flow of current since this might polarize an electrode. Voltammetry differs from coulometry in the respect that with the latter, measures are taken to minimize or compensate for the effects of concentration polarization. Furthermore, in Voltammetry a minimal consumption of analyte takes place, whereas in coulometry essentially all of the analyte is converted to another state.

Polarography is that branch of Voltammetry in which changes in current, resulting from the electrolysis of the solution under study are
investigated using a renewable mercury droplet as the indicator electrode (cathode). The anode of the electrolytic cell called the reference electrode consists of either a mercury pool at the bottom of the cell or a calomel electrode.

The theory and technique of Polarography have been developed only long time after Palmaer used the dropping mercury electrode in 1898. It was only in 1922, that Jaroslav Herovsky studied the characteristics of voltage-current curves obtained in the electrolysis of substances at the dropping mercury electrode under conditions of concentration polarization. Later, he was awarded a Nobel Prize in 1959 in recognition of its importance.

Polarography is an electrochemical method of analysis incorporating features of electrolysis but distinct from it. In electrolysis the aim is to remove completely a chosen constituent from the solution by passing an electric current through it for a sufficient length of time. The electrodes have relatively large surfaces and the solution is stirred to facilitate transport of electroactive material to the electrode. In contrast to this, the electrolysis in Polarography is of short duration and the electrode on which the constituents are placed out is a dropping mercury electrode or other micro electrode so that the currents are very small. Hence the changes produced by Polarography are normally (with 5 to 20ml test solution) not measurable, and the polarographic solution can be recovered virtually unchanged.

The electro chemical technique Polarography used in analytical chemistry, involves measurements of current-voltage curves, obtained when
voltage is applied to electrodes immersed in the solution being investigated. One of the electrodes is an indicator electrode. It is a dropping mercury electrode, consisting of a mercury drop hanging at the orifice of a fine bore glass capillary. The capillary is connected to a mercury reservoir so that mercury flows through the capillary at the rate of a few milligrams per second. The lifetime of each drop is usually 3 to 5 seconds. Each drop forms a new electrode; its surface is practically unaffected by processes taking place on the previous drop. Hence, each drop represents a well-reproducible electrode with fresh clean surface. The second electrode is a reference electrode; its potential remains constant during the measurement. The potential at the indicator electrode varies in the course of measurement of the current-voltage curve, because of the change of the applied voltage.

In view of the relative surface areas of the two electrodes, it follows that at the large auxiliary electrode the current density will be very small, while at the working electrode, it is hundreds of time higher. In consequence, the large or the counter electrode is not readily polarized and when small currents flow through the cell, the concentration of the ions in the electrode layer (i.e., the layer of solution immediately adjacent to the electrode) remains virtually equal to the concentration in the bulk solution and the potential of the electrode is maintained at a constant value. By contrast, at the micro electrode, the high current density causes its potential to deviate considerably from the equilibrium value (i.e., it assumes any potential applied to it from an external source the micro electrode is then said to be polarized) and consequently the electrode layer tends to become depleted of the ions being discharged at the electrode and if the solution is not stirred, then the diffusion of ions across the
resultant concentration gradient takes place. The working electrode being perfectly polarisable assumes the correspondingly increasing negative potential applied to it; very small current flows in the cell until the decomposition potential is reached. As the cathode potential is made progressively more negative, than the decomposition potential, current suddenly commences to increase until the current approaches a steady limiting value. Inspite of the fact that the reducible ion in the bulk of the solution diffuses slowly towards the electrode, a point is reached where the reducible ion or compound is nearly depleted at the electrode, a further increase in e.m.f. causes practically no increase in current unless a second compound able to depolarize the working electrode is present in the solution. A polarogram can be plotted between the current flowing through the polarographic cell against the increasing potential of the dropping electrode. A typical polarogram is depicted in Fig. 1.

The virtually flat upper portion of the polarographic wave is called its plateau and the total current which flows through the cell at a potential on the plateau is called the limiting current of the substance responsible for the wave. The difference between the limiting current and residual is called the diffusion current or wave height \( i_d \) of that substance and is a function of the concentration of the electroactive material. The potential at which the current is one-half of the diffusion current is called half-wave potential designated as \( E_{1/2} \). The half-wave potential of a reducible substance is independent of concentration and is the characteristic of the nature of the reacting material. This is the essential basis of quantitative and qualitative polarographic
Fig. 1: Typical polarogram obtained with the dropping mercury electrode.
analysis. A schematic diagram of a simple polarographic set up is shown in Fig. 2.

The success of polarography was largely attributed to the fact that the dropping mercury electrode has several advantages over solid metal such as platinum as an indicator electrode. One of the most important of these is the high over potential for the evolution of hydrogen on mercury. This makes it possible to study the reductions of many substances including even the alkali and alkaline earth metal ions, which could not possibly be deposited onto a platinum cathode without interference from the simultaneous reduction of water or hydrogen ion. Unlike a solid electrode, a mercury droplet has a perfectly smooth surface free from scratches or any other irregularities; this makes the accurate calculation of the electrode area a rather simple matter. Since, a fresh surface of the electrode is renewed regularly; absorbed or deposited materials cannot accumulate on the electrode surface. Hence numerous metals which are soluble in mercury electrode only negligibly small quantities of the substance are deposited in the vicinity of dropping electrode. For this reason there is no depletion of the depolarizer in the solution and provided the volume of the electrolyzed solution is not too small, even after several runs the curves obtained are identical. Finally, the dropping mercury electrode is much less sensitive to mechanical disturbances than a stationary solid microelectrode because a shock which would cause the latter to vibrate for sometime merely dislodges one drop prematurely from a dropping electrode without having much effect on the next. An even more serious defect of a stationary solid micro electrode is that the concentration gradient resulting from the flow of current extends further and further out into the
Fig. 2: Schematic diagram of essentials for polarographic analysis.

DME: Dropping Mercury Electrode; T.S: Test solution; J: Agar bridge;
SCE: Saturated Calomel Half-cell; P: Potentiometer or Polarography;
B: Battery; G: Galvanometer; h: Height of Mercury Column.
solution as time goes on, so that ions must diffuse through a greater and greater distance to reach the electrode surface, resulting in a steady decrease of the current.

On the other hand, there are certain definite limitations associated with the dropping electrode. The dropping mercury electrode may be applied over the range +0.4 to about -2.0 volts with reference to S.C.E. At about +0.4 volt mercury dissolves and gives an anodic wave; it begins to oxidize to mercury (I) ion. At potentials more negative than about -1.8 Volts vs S.C.E., visible hydrogen evolution occurs in acid solutions and the usual supporting electrolytes commence to discharge. The range may be extended to about -2.6 Volts vs S.C.E. by using supporting electrolytes having higher reduction potentials than the alkali metals. For work at potentials where mercury undergoes oxidation, other types of electrodes must, therefore, be sought.

From the stand point of analytical chemistry, the sensitivity of polarography is restricted by the charging current caused by the growth of the drop. From the theoretical point of view a serious complication in the mathematical formulation is introduced by the necessity of considering the growth of the drop. The current varies between a minimum and maximum for each drop of mercury it forms, since there is periodic change in the surface area of the drop. Therefore, the graph lines obtained are actually not smooth lines but are saw toothed lines. The amplitude of the fluctuation is small; however, smooth lines can easily be drawn between them to represent the average current during the drop life.
POLAROGRAPHIC CURRENTS

The total current that flow in, consists of the following components:

a) Residual Current,

b) Migration Current and

c) Diffusion Current.

a) Residual Current

The current that flows in the absence of the depolarizer (i.e. due to the supporting electrolyte) is called residual current. This has to be taken into consideration while interpreting the polarograms.

b) Migration Current

It is the current due to migration of ions caused by the electrostatic field between the two polarographic electrodes. The contribution of this component is minimized under experimental conditions by taking large concentrations of the supporting electrolyte. Under these conditions, only ions of the supporting electrolyte migrate in electrostatic field. The ions of the depolarizer do not take part in migration. They reach the surface of the electrode by the process of diffusion.

c) Diffusion Current

Diffusion current is due to electroactive substances. When the potential of the DME is in the plateau region the electroactive ions or molecules are reduced or oxidized as soon as they reach the electrode surface. As a result they are consumed and their concentration in a thin layer of solution in contact with the electrode becomes zero. Now, there is a
concentration gradient of the depolarizer in the solution and the electroactive ions or molecules diffuse towards the drop from adjacent layers a little further away from the electrode resulting in the limiting current. When the mercury drop falls, the solution rushes into that space and the concentration gradient disappears when a new drop is formed, diffusion takes place again at the same rate as described earlier. The average current during the life time of each drop is the same and thus it leads to the flat plateau on the polarogram.

The limiting current of a wave is very important and is called diffusion current as it reflects the rate at which the ions or molecules of the depolarizer reach the electrode surface under the influence of a diffusion force. The basis for the quantitative polarographic analysis is the existence of the linear proportionality between the diffusion current and the concentration of the depolarizer as given by Ilkovic equation.

\[ i_d = 607 \times 10^{-6} n D^{1/2} C m^{2/3} t^{1/6} \]  

where,

- \( i_d \) = Average diffusion current, \( \mu A \) (10\(^{-6}\) amps)
- \( n \) = Number of Faradays per mol involved in the electrode reaction
- \( D \) = Diffusion coefficient of the electroactive material, (cm\(^2\)/sec)
- \( C \) = Concentration of the electroactive material, (millimoles/litre).
- \( m \) = rate of flow of mercury through the capillary, (mg/sec).
- \( t \) = time between successive drops of mercury, (in seconds).
The terms \( m^{2/3} \) and \( t^{1/6} \) are dependent on the character and size of the capillary, the terms, \( n \), \( C \) and \( D^{1/2} \) are determined by the properties of the solute and solution.

Sometimes the factors pertaining to any one electrode process under a fixed set of experimental conditions (supporting electrolyte composition, \( E_{d.e.} \), temperature etc.) the quantities '\( n \)' and '\( D \)' in the Ilkovic equation are fixed for any reducible ion or molecule. However, \( C \), \( m \) and '\( t \)' can all be varied. It is, therefore, convenient to rewrite the Ilkovic equation in the form:

\[
I_d = \frac{607 nD^{1/2}}{C m^{2/3} t^{1/6}}
\]

The quantity ‘\( I_d \)' defined by this equation is called the 'diffusion current constant' and it has a characteristic value for any one electrode process occurring under any defined set of experimental conditions.

The diffusion current is dependent on number of factors including the diffusion coefficient of the depolarizing substance and its concentration in the bulk of the solution, number of Faradays consumed in one mole of the electrode reaction, the area of the electrode and the transfer coefficient.

The Ilkovic equation is valid only if the wave obtained is solely due to diffusion of ions from the bulk of the solution to the electrode surface. This equation fails if the wave obtained is partly or wholly controlled by the kinetics of the reaction, the presence of catalytically active substances in solution or the adsorption or either the oxidized or reduced ion or groups on the surface...
of mercury drop. So the validity of this equation is decided by considering whether the polarographic wave obtained, is diffusion controlled or not. To decide this following factors are considered.

(1) The diffusion current $i_d$ is proportional to $m^{2/3} t^{1/6}$ when the other factors in the Ilkovic equation are constant. The drop time 't' depends upon the heights of mercury column. Hence, if the wave is diffusion controlled $K = i_d / \sqrt{h_{Hg}}$. This is the frequently used method of ascertaining whether the height of the wave is diffusion controlled or not. If 'K' is not constant within the limits of experimental error over a wide range of the mercury heights it may be concluded that the current must be either partly or wholly governed by the rate of some process other than the diffusion of metal ions.

(2) 'D' is the diffusion coefficient in the Ilkovic equation is given by the Nernst equation as:

$$D = \frac{RT}{zF^2} \lambda_a$$

.....(3)

where

- $R$ = the gas constant in volt-coulombs per degree
- $T$ = absolute temperature
- $\lambda_a$ = the equivalent conductivity at infinite dilution
- $Z$ = the charge of the ion
- $F$ = the number of coulombs per Faraday

The conductivity of the solution varies rapidly with temperature causing changes in D and hence in value $i_d$. Normally $D$ and $i_d$ values increase by 2
and 3 percent respectively per degree rise in temperature. High deviations from these values are common tests for kinetic and catalytic currents.

(3) When other factors in the IIkovic equation remain constant the diffusion current $i_d$ is directly proportional to the concentration of the reducible or oxidisable substances. Hence a graph plotted between the diffusion current and concentration of the substance should give a straight line if the wave is diffusion controlled. This forms the quantitative aspect of polarography.

Complexation of a metal ion decreases the diffusion current if the ligand is bigger in size to the water molecules it replaces and shifts the half-wave potential generally to the more cathodic value. These two variables induced by increasing concentration of ligand allows the determination of coordination number, size and stability constants of complexes in solution or serve to elucidate the kinetics of the rate determining step depending upon the type of the electrode reaction.

**Oxygen removal**

Dissolved oxygen undergoes a two-step irreversible reduction at the dropping electrode; the $\text{H}_2\text{O}_2$ produced in the first step is reduced to $\text{H}_2\text{O}$ in the second. The two waves of equal size result, the first with a half-wave potential at about -0.14 V and the second at about -0.9 V vs SCE. The two half-reactions are somewhat slow. As a consequence, the waves are drawn out over a considerable potential range. While these polarographic waves are convenient for the determination of oxygen in solutions, the presence of this
element often interferes with the accurate determination of other species. Thus, gas accomplishes this end. A stream of the same gas, usually nitrogen, is passed over the surface during the analysis to prevent re-absorption.

**Nature of the Limiting Current**

Besides diffusion currents, the limiting current is classified on the basis of the nature of the process governing it as 1) Kinetic currents, 2) Catalytic currents and 3) Adsorption currents.

**Kinetic currents**

If the rate of the chemical reaction partly or completely governs the height of the polarographic wave (limiting current), it is referred to as a 'kinetic wave'. These types of the waves follow the general mechanism as mentioned below.

\[
\begin{align*}
  Y & \overset{K_f}{\rightleftharpoons} O \\
  O + ne & \rightarrow R
\end{align*}
\]

\[.....(i)\]

\[.....(ii)\]

In the above equation 'O' is reducible at potentials where 'Y' is not. But in some systems it is possible to reduce 'Y' directly at a more negative potential than is needed to reduce 'O'. \(K_f\) and \(K_r\) are the psuedo first order rate constants for the forward and reverse reaction.

The mathematical expression relating the kinetic limiting current with concentration of the depolarizer is given as

\[
i_k = 493 \ n \ D^{1/2} \ C_y \ m^{2/3} \ t^{2/3} \ (K_f / K_b)^{1/2}
\]

\[.....(4)\]
where

\[ i_k = \text{average kinetic current during the life of the drop} \]
\[ D = \text{diffusion coefficient of 'Y' or 'O'} \]
\[ C_y = \text{concentration of 'Y' in millimoles per litre} \]
\[ n = \text{number of electrons transferred} \]
\[ m = \text{mass of the drop in milligram} \]
\[ t = \text{drop time in seconds}. \]

Kinetic waves generally have high temperature coefficient. The limiting current of a kinetic wave is independent of height of mercury column. The plot between the limiting current and the concentration of the depolarizer is linear, but this plot will not pass through the origin in case of kinetic waves.

Catalytic Current

The polarographic wave corresponding to the electrode process which follows the mechanism mentioned below is referred to as 'Catalytic Wave'.

\[ O + ne \rightleftharpoons R \quad \text{.....(iii)} \]
\[ R + Z \rightarrow O \quad \text{(Fast)} \quad \text{.....(iv)} \]

Where 'Z' is not reduced when present alone at the electrode in the potential range of study. However, it is reduced by the reduction product 'R' to regenerate the electroactive substance 'O'. Thus the second step takes place a number of times during the life of the drop and is responsible for the great increase in the limiting current. The average catalytic current during the life of a drop is represented by the equation

\[ i_c = 493nD^{1/2} C_o m^{2/3} t^{1/6} \left[ \left( K_f + K_r \right) C Z O \right]^{1/2} \quad \text{.....(5)} \]
Where \( C_0 \) is the concentration of 'O' expressed in millimoles per litre.

An equation relating the rate constant and limiting current can be given as

\[
i_c = \frac{1}{5} \left( 1.255 \times 10^6 \right) n m^{2/3} t^{1/6} D^{1/2} C_0 C_z^{1/2} K^{1/2} \ldots (6)
\]

where

- \( i_c \) = average catalytic current
- \( n \) = number of electrons
- \( D \) = polarographic diffusion coefficient of the depolarizer 'O'
- \( C_0 \) = concentration of the electro active species in millimoles per litre
- \( C_z \) = concentration of the electro-inactive species (z) in the given potential range expressed in millimoles per litre.
- \( K \) = rate constant of the reaction producing the electroactive species.

Catalytic currents being a special case of kinetic currents possess the same characteristics as those of kinetic currents.

**Adsorption currents**

If either the electroactive species (or) the product of the electrode reaction is adsorbed on the surface of the drop, adsorption currents are observed. Suppose the product 'R' of the electrode reaction is adsorbed, a single wave representing

\[
O + ne \rightleftharpoons R \ldots (v)
\]
the reduction of 'O' to adsorbed 'R' is noticed at low concentration of 'O'. The wave in such cases is still diffusion controlled and its height is proportional to the concentration of 'O'. As the concentration of 'O' increases, a point will be reached at which enough of 'R' is formed during the life of the drop to cover its entire surface. Beyond this point the excess 'O' added is reduced to 'R' in the dissolved state at a more negative potential resulting in the appearance of a second wave. The first wave is called the 'adsorption wave', and the second 'the normal wave'. The total height of the double wave corresponds to the reduction of all of the 'O' diffusing to the surface of the drop and is therefore diffusion controlled and its height is proportional to the concentration of 'O' and $h^{1/2}$. None of these things is true of either of the waves individually.

If on the other hand 'O' is adsorbed and 'R' is not, the single wave obtained at low concentration of 'O' will represent the reduction of adsorbed 'O'. On increasing the concentration of 'O' this wave will reach a limiting height when the amount of 'O' diffusing to the surface of each drop is just sufficient to cover the entire surface of the drop. At still higher concentrations the excess 'O' remaining dissolved at the drop surface will produce a normal wave at a less positive potential.

The limiting height of the adsorption wave is proportional to the number of molecules adsorbed on the drop during its life. Average adsorption current $i_a$ is expressed as

$$i_a = 13.66 n m^{2/3} r^{-1/3} / a$$

.....(7)
Where 'a' is the area covered by each molecule. Adsorption waves are observed with methylene blue, thiols, organic mercury compounds, uracils and arsenic.

**Polarographic Maxima**

An increase of current above the limiting value in the form of a maximum is often noticed on polarographic waves. The origin of the maximum is sometimes connected with the mechanism of the electrode process as in the case of catalytic discharge of ions, while in many cases, it is caused by the increased transport of the depolarizer towards the electrode by a streaming motion of the solution. The later is more frequent and is called the streaming maximum. These are further divided into two types namely (1) Maxima of the first kind and (2) Maxima of the second kind.

**Maxima of first kind**

In dilute solutions of supporting electrolytes this kind of maxima is usually observed on the rising portion of the polarographic wave. It increases rapidly with voltage to larger values than limiting current and falls discontinuously to the normal limiting current. Thus first kind of maxima is characterized by a sharp current peak. The maximum is called positive or negative depending on whether the half-wave potential of the depolarizer lies on the positive side of the electro capillary curve or on the negative side.

Antweiler explained that streaming of the solution past the electrode surface causes this maxima. The direction of streaming is different for positive and negative maxima. In the case of positive maxima, the solution streams
from the neck to the bottom of the mercury drop while the streaming from the bulk of the solution towards the bottom of the drop occurs in negative maxima (Fig. 3).

The height of the maximum of the first kind is very sensitive to the presence of surface active substances such as dyes, terpenes and detergents, cellulose derivatives and colloidal substances. Gelatin is generally used to suppress the maximum. The concentration of the maximum suppressor required should be carefully chosen depending on the concentration and nature of the depolarizer because any slight excess than required may affect the electrode process and may cause a shift or change in the polarographic wave.

**Streaming maxima of the second kind**

Streaming maxima of the second kind is usually observed in concentrated solutions of the supporting electrolyte (above 0.1 N). This appears on the limiting current region and it depends on the purity of the solution. This maximum appears as an increase in the original wave or forms a new wave and current does not fall abruptly in contrast to the first kind of maxima. The occurrence of maximum of second kind depends on the mercury flow rate. By reducing the mercury flow rate the maximum can be suppressed. This maximum is also sensitive to the presence of surface active substances. The maximum of the second kind is not observed with stationary electrodes. The increase of the current due to the maximum of the second kind is accompanied by the streaming of the solution around the dropping electrode. The direction of this streaming is always from the bulk of the solution towards
Fig. 3: Streaming in a drop and in the adjacent layer upon appearance of positive (a) and negative (b) polarographic maxima.
the bottom of the drop over the mercury surface to the neck of the drop and from there horizontally along the tip of the capillary into the solution (Fig. 4). The intensity of this motion attains its maximum value at the potential of the electro capillary zero and slowly decreases with the distance from this potential.

Maxima connected with the mechanism of the electrode process

There are cases in which the occurrence of the maximum cannot be explained due to the streaming effect but may be due to some electrode process. It may be of catalytic origin. A minimum or decrease in the current is sometimes observed in the reduction of anions, and the shape of the wave may be similar to those for the maxima. Sometimes a maximum occurs due to the evolution of gas bubbles mostly of hydrogen.

A decrease in the current may also be observed when the reaction product forms a film at the electrode surface. The dependence on the height of the mercury reservoir is not uniform and usually gives little information about the character of the maximum.

Reversible and Irreversible processes

Electrode reactions at d.m.e. can be broadly divided into reversible and irreversible processes. Reversible reactions are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. On the other hand irreversible reactions are so slow that they precede only a fraction of the way towards equilibrium during the life of each drop. For these reactions it is the rate of the electron transfer process and the
Fig. 4: Streaming inside a drop during its formation.
manner in which this is influenced by the electrode potential that governs the relationship between the current and potential. Between these two electrode reactions there is an intermediate class of reactions that are fast enough to approach the equilibrium during the drop life but not quite so fast that they appear to reach it within the experimental error of the measurements. These types of electrode reactions are known as quasi-reversible reactions. The values of standard rate constant, $K_s$ of these three types of reactions are given as follows:

1. Reversible processes where $K_s > 2 \times 10^{-2} \text{ cm sec}^{-1}$
2. Irreversible process $K_s < 10^{-5} \text{ cm sec}^{-1}$
3. Quasi-reversible process $K_s = 2 \times 10^{-2} \text{ to } 10^{-5} \text{ cm sec}^{-1}$

The theory of reversible processes was well-established in the early stages of the development of the field.

**Reversible electrode reactions at d.m.e.**

Consider a reduction reaction occurring at the dropping mercury electrode which may be represented as

$$\text{Oxidant} + n \text{ electrons} \stackrel{\text{Reductant}}{\rightleftharpoons} \text{Ox} + n\text{e} \stackrel{\text{Red}}{\rightleftharpoons} \text{Red} \quad \ldots \quad (8)$$

When the oxidized species is brought to the electrode surface it can be reduced at a proper potential. The transfer of the species is due to the three modes of transfer viz., migration, convection and diffusion. Diffusion becomes the sole mode of transfer, convection and migration being avoided. The current depends upon the kinetics of the electrochemical reaction and on the
rate of mass transfer to the electrode surface. When this reaction is rapid and
chemical equilibrium is attained at the electrode, the process becomes
reversible, and Nernst equation can be applied. Then the potential of the
electrode is given as

\[ E = E^\circ - \frac{RT}{nF} \ln \frac{a_R^o}{a_O^o} \]  

\[ \ldots \ldots (9) \]

Where \( E^\circ \) is the standard potential, \( a_R^o \) and \( a_O^o \) are the activities of the
species at the electrode surface correlating \( E, E_{1/2} \), the half-wave potential, \( i \),
the current at potential \( E \) and \( i_d \) diffusion current. Heyrovsky and Ilkovic
derived the equation as

\[ E = E^\circ - \frac{RT}{nF} \ln \left( \frac{D_o}{D_n} \right)^{1/2} \]  

\[ \ldots \ldots (10) \]

and

\[ E_{d.m.e} = E_{1/2} - \frac{RT}{nF} \ln \frac{i_d}{i_d - i} \]  

\[ \ldots \ldots (11) \]

\[ E_{d.m.e} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \]  

\[ \ldots \ldots (12) \]

Where

\[ E_{d.m.e} = \text{Applied potential of the dropping mercury electrode} \]

\[ E_{1/2} = \text{Half-wave potential of the depolarizer} \]

\[ i = \text{Mean current at the applied potential} \]

\[ i_d = \text{The diffusion current} \]

\[ n = \text{Number of electrons involved in the process} \]

\[ F = \text{Faraday} \]
The above equation indicates that a plot of $\log\left(\frac{i}{i_d - i}\right)$ vs E should give a straight line with slope equal to $\frac{0.0591}{n}$ volts which is the most common criterion for the thermodynamic reversibility. The intercept on the x-axis gives the half-wave potential, $E_{1/2}$. Even though this linear relationship is usually taken as an important criterion for establishing reversibility of the polarographic process it should be used with great caution. Very often a linear plot is obtained for processes classified as irreversible. However, in such a process the value of $n$ is non-integer. Sometimes the observed slope of such a plot for a reversible wave may differ from theoretical value by 3-5 mV but any difference is greater than this is a proof for irreversibility. The diffusion coefficients of the oxidized $D_o$ and reduced species $D_R$ are very nearly same in number of cases. Therefore, it follows from equation (3) that the half-wave potential in the case of reversible processes is identical with the standard potential of the system.

The other factors which can be considered to decide the reversibility of an electrode process are given below. Tomes method requires the measurement of $E_{3/4}$ and $E_{1/4}$ i.e. the potentials at which the current is equal to three-fourths and one-fourths of the diffusion current. At $E_{1/4}$, we have

$$E_{1/4} = E_{1/2} - \frac{0.0591}{n} \log \frac{i_d / 4}{i_d - i_d / 4}$$  \hspace{1cm} ...(13)

$$= E_{1/2} - \frac{0.0591}{n} \log \frac{1}{3}$$  \hspace{1cm} ...(14)
And at

\[ E_{3/4} = E_{1/2} - \frac{0.0591}{n} \log 3 \]  

...(15)

So that

\[ E_{3/4} - E_{1/4} = -\frac{0.0591}{n} \log 9 \]  

...(16)

\[ = -\frac{0.0564}{n} \]  

...(17)

Hence for a reversible electrode reaction

\[ E_{3/4} - E_{1/4} \text{ must be equal to } -\frac{0.0564}{n} \]

The half-wave potential of reversible wave is independent of the concentration of the substance being reduced or oxidized. An appreciable variation of \( E_{1/2} \) with concentration is a proof of irreversibility of the reaction. The reverse is not true, however, for the half-wave potential of many irreversible waves are also independent of concentration.

The most conclusive proof of reversibility of a reaction is secured when polarograms of solutions containing the reduced form of redox couple involved in the reaction are found to give anodic waves whose half-wave potentials are identical with the cathodic half-wave potentials of the oxidized form. This is the same thing as securing a composite wave with no inflection around the residual current curve with a solution containing both the oxidized and the reduced forms. It is worthwhile to make sure that the cathodic and anodic \( i_a \)'s obtained with equal concentrations of the reduced and oxidized species are approximately equal. In such a case the point of
inflection is the redox potential of the system. In addition to these common criteria of reversibility there are several others that are less often used, partly because special information must be obtained to permit their application and the important one among these is temperature coefficient values. The temperature coefficients of a reversible wave depend on the nature of the electrode reaction. For a reduction to a metal soluble in mercury \( \frac{dE_{1/2}}{dt} \) is about \(-0.7\) mV/degree and for a homogeneous reduction \( \frac{dE_{1/2}}{dt} \) may be either positive or negative but is rarely greater than \( \pm 1\) mV/degree. The temperature coefficient of \( E_{1/2} \) for an irreversible wave is almost always positive and is usually of the order of several mV/degree. Larger temperature coefficients of \( E_{1/2} \) constitute fair evidence against the reversibility of the wave.

**Applications of Polarography**

Polarographic analyses can be used directly for the determination of any substance solid, liquid, or gaseous, organic or inorganic, ionic or molecular that can be reduced or oxidized at dropping mercury electrode. One of the most important advantages of polarography is the determination of two or more substances by obtaining a single current-potential curve. Another important technique is the Amperometric titration which involves polarographic measurements. In addition to analytical uses, polarography is one of the most fruitful techniques of research in physical, inorganic and organic chemistry. This technique is spreading more widely in subsidiary fields like biochemistry, pharmaceutical chemistry, environmental chemistry and others. It is being used to study diverse topics as hydrolysis, solubility, complex formation, and
adsorption, the stoichiometry and kinetics of chemical reactions, the mechanisms of electrode reaction and of chemical reactions accompanying them, standard and formal potentials, molecular dimensions, the effects of structure on reactivity and many others of interest and importance.

In electrochemistry polarography allows measurement of potentials and yields information about the rate of the electrode process, adsorption desorption phenomena, and fast chemical reactions accompanying the electron transfer. Since polarographic experiments are simple and not too time consuming, polarography can be used in a preliminary test designed to find the most suitable model compound for detailed electrochemical investigations.

In fundamental applications, polarography allows one to distinguish the form and charge of the species (for example, inorganic complex or organic ion) in the solution. Polarography also permits the study of equilibria (complex formation, acid-base, tautomeric) rates and mechanisms. For equilibria established in the bulk of the solution in more than 15 second, measurement of wave heights of individual components makes possible the evaluation of equilibrium constants. For equilibria that are very rapidly established at the electrode surface, equilibrium constants can be determined from shifts of half-wave potentials. Finally for some equilibria between these two extremes, which are established in times comparable to the drop time (3 seconds), calculation of rate constants is possible. In this way, rate constants of very fast reactions of the order $10^5 - 10^{10}$ litre mole$^{-1}$ sec$^{-1}$ can be determined.
For slower reactions, rate constants can be found from changes of wave heights with time. Moreover, as some reaction intermediates giving separate waves can be detected, identified and followed polarographically (if their half-lives are longer than 15 sec), Polarography can prove useful in mechanistic studies. Elimination of Mannich bases, hydration of multiple bonds in unsaturated ketones, and aldolization are example studies.

Polarography can be used for investigation of the relationship between electrochemical data and structure. Reduction of most organic systems, particularly in aqueous media, involves steps with high activation energy and is therefore irreversible. Half-wave potentials of such systems are a function of the rate constant of the electrode process. This heterogeneous rate constant is frequently influenced by structural effects, as are, in a similar manner, rate constants of homogeneous reactions. Therefore, effects of substituents on half-wave potentials in aromatic systems and in aliphatic systems can be treated by the Hammett relations and the Taft substituent constants respectively. Among steric effects, for example, steric hindrance of coplanarity or effects of cis-trans isomerism affect polarographic curves. Polarography also makes it possible to distinguish between some epimers, for example bearing axial or equatorial halogen.

In Inorganic analysis, Polarography is used predominantly for trace metal analysis (with increased sensitivity of differential Pulse Polarography and stripping analysis). The most important fields of application of inorganic determinations are in metallurgy, environmental analysis (air, water, and sea water contaminants), food analysis, toxicology and clinical analysis. The
possibility of being able to determine vitamins, alkaloids, hormones, terpenoid substances, and natural colorings substances has made polarography useful in analysis of biological systems. Analysis of drugs and pharmaceutical preparations, determination of pesticide or herbicide residues in the foods and so forth. Polarography can also make possible determination of monomers, catalysts and even some reactive groupings in polymers.
Section(ii): Reversible Electrode Reactions of Metal Complexes at D.M.E (Methods)

Cations bound in a complex can also be reduced to the metallic state or to a lower valency state as

\[ \text{M}^{n+} + ne \rightleftharpoons \text{M} \]  \hspace{1cm} (18)

\[ \text{M}^{n+} + xe \rightleftharpoons \text{M}^{(n-x)} \]  \hspace{1cm} (19)

The interpretation of the polarographic waves obtained for such reductions was discussed by Lingane [7] in a review article. In the presence of a complexing agent the characteristics of the polarographic reduction wave for metal ions in solution are altered in two distinct ways. Firstly, the half-wave potential is shifted usually to more negative values and secondly, the diffusion current becomes smaller. Generally this is ascribed to the more bulky nature of the complexed ion (compared to aqua metal ion) requiring more energy in order to undergo reduction process at the dropping mercury electrode. However, the electron exchange process remains relatively fast with respect to that of diffusion process so that the latter is still rate determining. This results in a reversible polarographic reduction of the complexed metal ion.

Measurement of shift in the half-wave potential as a function of concentration of ligand can be used to determine the formula and the stability constant of the complex. It should be emphasized that this information can only be obtained when the reduction or oxidation of the metal complex is reversible at the dropping mercury electrode.
Under these reactions two methods are discussed for the determination of stability constants and coordination number of metal complexes. The first one is that of Lingane, which is applicable to metal-ligand system in which a single complex species is formed to the virtual exclusion of all others over the entire ligand concentration working range. The second one is the DeFord and Hume [25] method for the study of consecutively formed complex ions, whose stabilities differ to such an extent from one another, that each tends to predominate between fairly and sharply defined limits of ligand concentration. It is a method of mathematical analysis of the shift of half-wave potentials with ligand concentration which makes possible the identification of successive complex ions formed and the evaluation of formation constants.

**Method of Lingane**

Lingane [7] has considered the case where reduction of the complex to the metal (soluble in mercury) at the dropping electrode. The electrode reaction for such reduction of a complexed one to metallic state is given as

\[ MX_j^{(n-j)m+} \rightleftharpoons M^{n+} + JX^m- \]

If these processes take place reversibly and much more rapidly than the rate of natural diffusion of ions to the electrode surface, then the potentials of the d.m.e. at all points on the polarographic wave may be given by

\[ E = E_A^0 - \frac{RT}{nF} \ln \frac{C_A^{2}y_A}{C_M^{2}y_M} \]  

...(21)
Where \( C_A^0 \) is the concentration of amalgam formed on the surface of the d.m.e. and \( \gamma_A \) its activity coefficient. \( C_M^0 \) is the concentration of the metal ion \( M \) in the solution at the drop surface and \( \gamma_M \) its activity coefficient, \( E_A^0 \) is the standard potential of the amalgam.

The overall thermodynamic stability constant, \( \beta_{MX_j} \) of the complex \( MX_j \) (charges are omitted for clarity) is given by

\[
\beta_{MX_j} = \frac{[MX_j]}{[M][X]^j} \quad \ldots(22)
\]

Where the terms in brackets represent activities. The concentration of the complex in the bulk of the solution, for a given concentration of metal ion and ligand, may then be written as

\[
C_{MX_j} = \frac{\beta_{MX_j} C_M \gamma_M [X]^j}{\gamma_{MX_j}} \quad \ldots(23)
\]

At the electrode surface the metal ion will have a concentration given by

\[
C_{MX_j}^0 = \frac{\beta_{MX_j} C_M^0 \gamma_M [X]^j}{\gamma_{MX_j}} \quad \ldots(24)
\]

Now substitution the value for \( C_M^0 \gamma_M \) from equation (24) into equation (21), we have

\[
E = E_A^0 - \frac{RT}{nF} \ln \frac{C_A^0 \gamma_A \beta_{MX_j} [X]^j}{\gamma_{MX_j} C_{MX_j}^0} \quad \ldots(25)
\]
If the complexed ions arrive at the electrode by diffusion only, the mean current at any part of the reduction wave may be given by

\[ i = k_l M_{X_j} (C_{X_j} - C_{0M_{X_j}}) \]  \hspace{2cm} (26)

where \( k \) and \( l_{M_{X_j}} \) are the capillary constant (\( m^{2/3} \ t^{1/6} \)), and the diffusion current constant (\( 607 \ n \ D^{1/2} \)) of the species \( M_{X_j} \) respectively. The limiting mean current value as \( C_{0M_{X_j}} \) approaches zero, will be given by

\[ i_d = k_l M_{X_j} C_{M_{X_j}} \]  \hspace{2cm} (27)

A similar relation holds in terms of the concentration of metal atoms within the mercury, namely,

\[ i = k_l A C_{0A} \]  \hspace{2cm} (28)

where \( I_A \) is the diffusion current constant of metal atoms in the amalgam.

Substituting the value for \( C_{0A} \) from equation (28) into (25) gives

\[ E = E^o - \frac{RT}{nF} \ln \frac{i y_{A} \beta_{M_{X_j}} [X]^j}{k_l A \gamma_{M_{X_j}} C_{M_{X_j}}^{o}} \]  \hspace{2cm} (29)

From equations (26) and (27) we have

\[ C_{M_{X_j}}^{o} = \frac{i_d - i}{k l_{M_{X_j}}} \]  \hspace{2cm} (30)

Substituting for equation (30) into equation (29) we have

\[ E = E^o - \frac{RT}{nF} \ln \frac{i_{M_{X_j}} y_{A} \left( \frac{i}{i_d - i} \right) \beta_{M_{X_j}} [X]^j}{\gamma_{M_{X_j}}} \]  \hspace{2cm} (31)
By substituting the condition $i = \frac{i_d}{2}$, the expression for half-wave potential of reduction wave for the complex ion

$$\left( E_{1/2} \right)_C = E^0_A - \frac{RT}{nF} \ln \frac{I_{MX_j}}{I_A} \frac{\beta_{MX_j}}{\gamma_{MX_j}} \left( X \right)^j \quad \ldots (32)$$

The corresponding equation for the half-wave potential of a simple metal ion is given by

$$\left( E_{1/2} \right)_S = E^0_A - \frac{RT}{nF} \ln \frac{I_M}{\gamma_M} \frac{I_{MX_j}}{I_A} \quad \ldots (33)$$

Thus, the shift in half-wave potential, produced by the presence of an excess of ligand, can be represented by the

$$\left( E_{1/2} \right)_S - \left( E_{1/2} \right)_C = \Delta E_{1/2}$$

$$= \frac{2.303RT}{nF} \log \frac{\gamma_M}{\gamma_{MX_j}} \frac{I_{MX_j}}{I_M} \frac{\beta_{MX_j}}{\gamma_{MX_j}} \left( X \right)^j \quad \ldots (34)$$

Assuming the diffusion current constants $I_M$ and $I_{MX_j}$ to be approximately equal, and dropping the activity coefficients i.e., $\frac{\gamma_M}{\gamma_{MX_j}} \approx 1$, equation (34) can be simplified as

$$\Delta E_{1/2} = \frac{0.0591}{n} \log \beta_{MX_j} + j \frac{0.0591}{n} \log C_X \quad \ldots (35)$$

where $C_X$ refers to the analytical concentration of the ligand.

Equation (32) is written in the simplified form

$$\left( E_{1/2} \right)_C = E^0_A - \frac{0.0591}{n} \log \beta_{MX_j} - j \frac{0.0591}{n} \log C_X \quad \ldots (36)$$
Hence the rate of change of half-wave potential with ligand concentration may be expressed as

\[
\frac{d(E_{1/2})_c}{d \log C_x} = -j \frac{0.0591}{n} \quad \text{(At 25° C)} \quad \ldots(37)
\]

Thus, a plot of \((E_{1/2})_c\) vs \(\log C_x\) should be linear of slope 
\(-j\left(\frac{0.0591}{n}\right)\) from which the coordination number \(j\), of the complex, \(MX_j\) can be found. Substituting the value of \(j\) in equation (15) the stability constant \(\beta_{MX_j}\) can be determined.

The Lingane method can be successfully employed for the determination of stability constant \(\beta\) and the formula of the metal complex \((MX_j)\) in solution provided; the solution contains a single complex species or more complex species having stability constant differing by at least a power of 10.

**DeFord and Hume Method**

DeFord and Hume [25] developed a method for determining consecutive formation constants of complex ions from polarographic data. It is a method of mathematical analysis of the shift of half-wave potentials with ligand concentration which makes possible the identification of successive complex ions formed and the evaluation of formation constants.

The reduction process of the step-equilibria between successively formed complexes can be represented as
The concentration of each complex species, for a given free ligand concentration, is given by expressions of the form of equations (23) and (24). Here, however, equation (24) must be summed overall possible species, so that the equation (24) becomes

$$\sum_{o}^{M} C_{M}^{o} = C_{M}^{O} \sum_{o}^{N} \beta_{MX_{j}} \frac{[X]^{j}}{\gamma_{MX_{j}}}$$

...(39)

Here $j = 1, 2, 3, \ldots N$

So, equation (25) can be written as

$$E = E_{A}^{O} - \frac{RT}{nF} \ln \frac{\sum_{o}^{N} \beta_{MX_{j}} [X]^{j}}{\sum_{o}^{N} C_{MX_{j}}^{O} \gamma_{MX_{j}}}$$

...(40)

In terms of currents, equation of the form (6), (7) and (8) hold except that now the total current must be expressed in terms of the concentration from each species.

Thus

$$i = \sum_{o}^{M} i_{MX_{j}} = k \sum_{o}^{N} I_{MX_{j}} \left( C_{MX_{j}} - C_{MX_{j}}^{O} \right)$$

...(41)

Where $k$ is the capillary constant and $I_{MX_{j}}$ is the individual diffusion current constants. Alternatively,
\[ i = k \, I_C \sum_{j}^{N} (C_{MXj} - C_{MXj}^0) \] \hfill (42)

Where \( I_C \) is the experimental mean value of the diffusion current constant for the mixture of complexes which in terms of the value for each individual species, is expressed by

\[ I_C = \frac{\sum_{j}^{N} I_{MXj} \beta_{MXj} [X]^j}{\sum_{j}^{N} \beta_{MXj} [X]^j} \gamma_{MXj} \] \hfill (43)

Equation (11) becomes

\[ E = E_A^0 - \frac{RT}{nF} \ln \left( \frac{I_C}{I_A} \right) \frac{\gamma_A^i}{\gamma_{MXj}} \sum_{j}^{N} \beta_{MXj} [X]^j \] \hfill (44)

Thus shift in half-wave potential is

\[ \Delta E_{1/2} = \frac{2.303 RT}{nF} \log \left[ \frac{I_C}{I_M} \sum_{j}^{N} \beta_{MXj} [X]^j \right] \gamma_{MXj} \] \hfill (45)

Rearranging the equation in order to calculate the individual overall constants,

\[ F_0 [X] = \beta_0 + \beta_1 [X] \frac{\gamma_M \gamma_X}{\gamma_{MX}} + \beta_2 [X]^2 \frac{\gamma_M (\gamma_X)^2}{\gamma_{MX^2}} + \ldots + \beta_N [X]^N \frac{\gamma_M (\gamma_X)^N}{\gamma_{MX^N}} \]

\[ = \text{anti} \log \left( \frac{0.4343 nF}{RT} \Delta E_{1/2} + \log \frac{I_M}{I_C} \right) \] \hfill (46)

The symbol \( F_0 [X] \) is introduced for convenience to represent the experimentally measurable quality on the right-hand side of the equation.
Maintaining constant ionic strength, the activity coefficients in equation (46) may be dropped and the equation becomes

$$F_0[X] = 1 + \beta_1 [X] + \beta_2 [X]^2 + \ldots + \beta_N [X]^N \ldots (47)$$

After recording the shift in $E_{1/2}$ the various $F_0[X]$ functions are determined for each value of $[X]$.

In order to determine $\beta_1 - \ldots - \beta_M$ Leden's [8] extrapolation method is applied. It is apparent from equation (46) that a plot of $F_0[X]$ vs $[X]$ will be a steeply rising curve. However, as $[X]$ approaches zero the graph will have a limiting slope of $\beta_1$ and an intercept on the $F_0[X]$ axis, of 1. Thus a preliminary value of $\beta_1$ is obtained.

A new function $F_1 [X]$ is then defined as

$$F_1 [X] = \frac{F_0[X] - 1}{[X]} = \beta_1 + \beta_2 [X] + \ldots + \beta_N [X]^{N-1} \ldots (48)$$

The derived values of $F_1 [X]$ against corresponding values of $[X]$ can be plotted which will have a limiting slope of $\beta_2$, as $[X]$ tends to zero, and an intercept on the $F_1 [X]$ axis of $\beta_1$. Thus a confirmative estimation of $\beta_1$ is possible and in addition a preliminary value of $\beta_2$ is obtained. Similarly a function $F_2 [X]$ is defined as

$$F_2 [X] = \frac{F_1[X] - \beta_1}{[X]} = \beta_2 + \beta_3 [X] + \ldots + \beta_N [X]^{N-2} \ldots (49)$$
This procedure is followed until all N complexes have been accounted for. For the penultimate complex, $\text{MX}_{N-1}$

$$F_{(N-1)}[X] = \left[ \frac{F_{N-2}[X]}{[X]} - \beta_{N-2} \right] = \beta_{N-1} + \beta_N [X] \quad \ldots(50)$$

Here the plot of $F_{(N-1)}[X]$ vs $[X]$ will be a straight line indicating the formation of penultimate complex. The final function, $F_N[X]$, will be independent of ligand concentration and thus,

$$F_N[X] = \left[ \frac{F_{N-1}[X]}{[X]} - \beta_{N-1} \right] = \beta_N \quad \ldots(51)$$

So the plot will be a straight line, parallel to x-axis, giving the value of $\beta_N$.

The mathematical form of the DeFord and Hume method has several interesting consequences. It is observed that a plot of $F[X]$ vs $[X]$ for the last complex will be a straight line with a positive slope and all previous $F[X]$ function plots will show curvature. These characteristics aid in establishing the number of complex ions formed and also provide a qualitative check on the validity of data.

The application of the method requires that the concentration of complexing ligand must be large in comparison with the metal ion concentration. DeFord and Hume method is best suited for the study of series of complexes of moderate and comparable stability.
Section(iii): Irreversible Electrode Reactions of Metal Complexes At D.M.E. (Methods)

A polarographic process is termed irreversible when the electron exchange process is quite slow. Nevertheless the rate limiting step may still be a diffusion process. Such a process is referred to as irreversible diffusion controlled process. Nernst equation cannot be applied in the interpretation of current-potential curves which are irreversible. The half-wave potentials in case of irreversible waves are far different from the standard potentials depending upon \( \eta \), the over voltage which is equal to the potential at which the reaction occurs minus the potential calculated from Nernst equation.

The shapes of the polarograms expected for a reversible and an irreversible reduction are shown in Fig (5). In an irreversible process the current is controlled mainly by the electrode reaction rate over a large part of the curve. However, at more negative potentials the electrode reaction becomes quite rapid and consequently the diffusion process becomes rate determining. Thus the Ilkovic equation is equally applicable to the limiting currents of both reversible and irreversible processes. In the case of irreversible process the half-wave potentials corresponding to the two processes that is oxidation and reduction are quite distinct and lie on different sides of the standard potential \( E_0 \) of the depolarizer. The greater the degree of irreversibility the greater is the separation. On the other hand for reversible processes the cathodic and anodic half-wave potentials coincide.

In its simplest form the mechanism responsible for a totally irreversible wave may be described by the equation
Fig. 5: A reversible (I) and a totally irreversible wave (II)
The rates of forward reaction $k_f$ and the backward reaction $k_b$ are given by

$$ k_f = k_f^o e^{(-a_f E)} \quad \ldots (53) $$

$$ k_b = k_b^o e^{(1-a) f E} \quad \ldots (54) $$

where

$$ f = \frac{nF}{RT}; \quad E = \text{potential and } \alpha = \text{transfer coefficient}. $$

Superscript 'o' refers to the rate constant at $E = 0$. The standard rate constant is related to the individual rate constants as

$$ k_s = k_f^o e^{(-a_f E^o)} = k_b^o e^{[(1-a) f E^o]} \quad \ldots (55) $$

Hence

$$ k_f = k_s e^{(-a_f (E-E^o))} \quad \ldots (56) $$

and

$$ k_b = k_s e^{[(1-a) f (E-E^o)]} \quad \ldots (57) $$

$k_s$ is a fundamental parameter characteristic of the couple and it is the value of the $k_s$ that determines whether the half-reaction is reversible or irreversible.

For a totally irreversible process the rate of a reaction expressed in moles of the substance transformed per unit time per unit area is given by

$$ - \frac{dN_o}{dt} = k_f C_o^o - k_b C_x^o \quad \ldots (58) $$
The product of flux, the area of the electrode and number of Faradays involved in the reaction gives the average polarographic current ‘i’ which is given by the equation

\[ i = nFA (k_f C^{o}_{O} - k_b C^{o}_{R}) \]  \hspace{1cm} \text{(59)}

The concentration at the electrode surface can be obtained from Ilkovic equation

\[ i = (i_a)c - 607 n D_C^{1/2} C^{o}_{C} m^{2/3} t^{1/6} \]  \hspace{1cm} \text{(60)}
\[ = 607 n D_R^{1/2} C^{o}_{R} m^{2/3} t^{1/6} - (i_a)_{a} \]  \hspace{1cm} \text{(61)}

Though \( k_a \) is more useful for describing the behaviour of a particular couple, it is \( k^{o}_{f} \) (or \( k^{o}_{f,h} \)) that is more useful for comparing the behaviour of different totally irreversible couples. Moreover, it is impossible to calculate \( k_a \) unless the formal potential is known or can be calculated from data obtained on both the cathodic and anodic waves for a couple. And too often, however, the formal potential is unknown, and unless both the cathodic and anodic waves appear on polarograms there is no hope of calculating the formal potential of \( k_a \). Therefore, the parameter \( k^{o}_{f,h} \) has always been evaluated for irreversible waves from polarographic data.

For the determination of the transfer coefficient and the standard rate constant numerous methods are available of which Koutecky [29] and Meites and Israel [68] methods are important. The stability constants and ligand number of metal complexes which undergo irreversible reductions at the dropping mercury electrode can also be determined by Schwarzenbch [8, 13] and Ringbom and Eriksson methods [30,31].
Koutecky Method

The method of Koutecky is applicable to totally irreversible processes. By taking into account the growth of the mercury drop Koutecky [22,29] developed a rigorous treatment which is applicable to totally irreversible process.

Neglecting the effect of backward reaction the equation for a purely cathodic wave is given in the form (44)

\[ i_{irr} = i_{rev} \frac{F(X)}{1 + \exp f\eta} \]  \ ...(62)

Where \( F(\chi) \) is a function of \( \chi \) and

\[ \chi = \left( \frac{12\tau}{7D_o} \right)^{1/2} k_f \left( 1 + \exp f\eta \right) \]  \ ...(63)

where \( f = \frac{nF}{7D} \) and \( \eta = E - E_f^o \) and other terms have usual significance.

In case of totally irreversible waves (where \( \eta_{1/2} \) exceeds 200mV for a one electron reduction) \( \exp f\eta \) is negligible and equation (62) and (63) can be written as

\[ i_{irr} = i_{rev} F(\chi) \]  \ ...(64)

and

\[ \chi = \left( \frac{12\tau}{7D_o} \right)^{1/2} k_f \]  \ ...(65)
The correction factors for the curvature of the dropping mercury electrode was calculated by Koutecky and Cizek [22] and the more rigorous equation is

\[ \frac{i_{\text{irr}}}{i_{\text{rev}}} = F(X) - \xi H_c(\chi) = F'(\chi) \quad \ldots \ldots (66) \]

where

\[ \xi = 50.4 \, D^{1/2} \, \Gamma^{1/6} \, m^{-1/3} \quad \ldots \ldots (67) \]

From the known values of D, \( \Gamma \) and m, \( \xi \) can be calculated using the equation (67). Values of \( F(\chi) \) and \( H_c(\chi) \) calculated by Koutecky's and Cizek for assigned values of \( \chi \) are given for ready reference [22].

\( F'(\chi) \) can be calculated from the equation (66). Utilizing \( F'(\chi) \) and \( \xi \) values 'i' can then be obtained and the corresponding value of 'E' is read from the polarogram. The transfer coefficient and the rate constants for the forward reaction can be calculated from equation (65). The standard rate constant can be calculated from knowledge of standard potentials. A plot of \( \log k_f \) vs E should result in a straight line with a slope equal to -0.0591/an volt at 25°, from which the transfer coefficient can be calculated. Extrapolation to 0 V gives the value of \( k_f^0 \) and standard rate constant can be obtained at the standard potential.

**Meites and Israel Method**

For a totally irreversible process whose rate is governed by a single electron transfer were studied by several authors and equations for the polarographic current-potential curves were given. The most rigorous solution
was given by Koutecky [22,29]. Delahay and Strassner [23,24] devised a graphical method, which yielded essentially identical values for the parameters $\alpha n$ and $k_{l,h}^o$. From Koutecky's treatment, Kern [37] has shown that a plot of $E_{d,e}$ vs $\log i/i_d$ employing average currents in the log term should be linear with a slope of $-0.0591/\alpha n$ volt at $25^\circ C$. These results were accepted by some of the workers concerned with the subject [54, 63].

A simple and most vulnerable method was developed by Meites and Israel [68] by taking into account the numerical deductions from Koutecky's method. They have suggested the use of maximum current at the end of a drop life for the calculations of $\alpha n$ and $k_{l,h}^o$ from polarographic data. This procedure is more convenient in general and is better adapted to the particular case in which the drop time varies appreciably over the rising portion of the wave than the relationship based on average current that was deduced by Kern. The derivation of their equation is described below.

Koutecky gave values for the function $F(\chi)$ where $\chi$ and the subsidiary variable $\lambda$ that is used here for the sake of convenience are defined as

$$\lambda = \sqrt{\frac{7}{12} X} = k_{f,h} \frac{i^{1/2}}{D_o^{1/2}}$$ \hspace{1cm} ...(68)

Assuming that diffusion to the electrode surface to be linear, the value of $F(\chi)$ is equal to the ratio $\frac{i}{i_m}$ for a polarographic wave on which the current, $i$, is determined by the rate of a single-electron-transfer step. The quantity $i_m$ is the current that would flow at the same potential if the rate of over-all process
is strictly controlled by diffusion. Both $i$ and $i_\infty$ are defined as maximum currents during a drop life. Equation (68) can be given for totally irreversible process in which the rate of backward reaction is negligibly small over the entire rising portion of the wave. Then $i_\infty$ will be equal to the diffusion current $i_d$, when the potential first becomes sufficiently negative to cause $i'$ to deviate significantly from zero.

On neglecting changes in the structure of the electrical double layer

$$k_{f,h} = k_{f,h}^o e^{(-\alpha n FE/RT)} \quad \ldots (69)$$

which, when combined with equation (68), yields

$$E = \frac{0.434 RT}{\alpha n F} \log \frac{k_{f,h}^o i^{1/2}}{D_{o}^{1/2}} - \frac{0.434 RT}{n F} \log \lambda \ldots (70)$$

On the basis of the values given by Kouteck'y it may be shown that

$\log \lambda$ is a linear function of $\log i/i_d - i$ over nearly entire raising portion of the wave in which the straight line represents the equation

$$\log \lambda = -0.1300 + 0.9163 \log \frac{i}{i_d} - i \ldots (71)$$

On combining equations (70) and (71) it follows from Koutecky results that an irreversible wave of the above type must obey the equation (at $25^\circ C$)

$$E_{d,e} = \frac{0.05915}{\alpha n} \log \frac{1.349 k_{f,h}^o}{D_{o}^{1/2} i^{1/2}} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i} \ldots (72)$$
Hence if ‘t’ is constant and independent of potential, a plot of $E_{d,e}$ versus $\log \frac{i}{(i_d - i)}$ for such a wave should be linear and should have a slope equal to $-0.0542/\alpha n$ volt.

Then

$$E_{d,e} = E' - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i} \quad \text{...(73)}$$

$$E' = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{(1.349 k_{f,h}^{o} i^{1/2})}{D_{o}^{1/2}} \quad \text{...(74)}$$

In these equations both $E_{d,e}$ and $E'$ are referred with respect to SCE.

Meites and Israel observed that except in unusual circumstances a plot of $E_{d,e}$ vs $\log \frac{i}{(i_d - i)}$ will be linear over nearly the entire rising portion of the wave. It was also found that the slope of such a plot depends to some extent on drop time employed. Hence it was suggested by them that the use of the equation (73) in the form

$$E_{d,e} = E' - \frac{0.0542}{\alpha n} \left[ \log \frac{i}{(i_d - i)} - 0.546 \log i \right] \quad \text{...(75)}$$

is preferable, where

$$E' = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{1.349 k_{f,h}^{o}}{D_{o}^{1/2}} \quad \text{...(76)}$$

A plot of $E_{d,e}$ vs $\left[ \log \frac{i}{(i_d - i)} - 0.546 \log i \right]$ will have a slope of $-54.2/\alpha n$ mV, and an intercept where the quantity being plotted along the abscissa is zero which is equal to parameter $E'$ defined by the equation from which $k_{f,h}^{o}$ is calculated. The parameter $\alpha n$ is best obtained from the slope.

For waves occurring between ‘0’ and -1.0 volts vs SCE the variation in drop
time ‘t’ may generally be ignored but outside this region it becomes much larger and correction for ‘t’ is necessary.

The Method of Ringbom and Eriksson

This method \cite{30,31} also depends upon the availability of suitable indicator ion as in the case of Schwarzenbach method, which must undergo reversible reduction at a more positive potential than an ion whose complexes are to be studied. The method is applicable to systems characterized by a set of metal-ligand step equilibria and is based on half-wave potential measurements.

The main characteristic of a labile system of complexes is that a single polarographic wave is produced whose half-wave potential is shifted to more negative values as the concentration of added ligand increases. If the metal ion that is reversibly reduced is \( N \), then its half-wave potential will be shifted by a characteristic amount on addition of a specified amount of complexing agent.

If metal ions, \( M \), are then added to the system, they will compete with \( N \) for association with \( X \) thereby reducing the effective amount of ligand available for complexation with the indicator species. As a result, the half-wave potential for \( N \) will now correspond to a smaller value of the ligand concentration so that the observed \( E_{1/2} \) value will occur at a less negative potential than in the absence of \( M \). The concentration of the metal ion, \( M \), must be \( 10^3 \) times greater than that of \( N \) in order to make the change in shift measurable for practical purpose.
The practical procedure of this method involves mainly two stages. In the primary stage series of $\Delta E_{1/2}$ values are obtained for $N$ over a wide range of ligand concentration in fairly small increments. If the complexes formed in the $N, X$ system are relatively weak it may be assumed that the total analytical concentration may be identified with the free ligand concentration $[X]$. A graph may then be drawn of $\Delta E_{1/2}$ as a function of $[X]$.

The entire set of measurements are repeated in the presence of a fixed concentration of metal ion $M$ and the $\Delta E_{1/2}$ values are computed. In each case the $\Delta E_{1/2}$ value will be less than the value for the indicator system alone, and a plot of $\Delta E_{1/2}$ versus $[X]$ will be below that for the first curve and at higher values of $[X]$, it will become parallel indicating attainment of the maximum coordination number of the system, $M, X$. The above plot is utilized in determining the free ligand concentration for the system $M, X$ at any value of known total ligand concentration. The ligand number $n'$ may be evaluated as follows:

The ligand number $n'$ of the system, $N, X$ is defined as

$$\bar{n}' = \frac{\text{total concentration of } X \text{ bound to } N}{\text{total concentration of } N}$$

...(77)

$$= \frac{C_X - [X]}{C_N}$$

When $M$ is also present, the ligand number $\bar{n}$ of the system $M, X$ is given by

$$\bar{n} = \frac{\text{Total concentration of } X \text{ bound to } M}{\text{Total concentration of } M}$$
\[
\text{Total ligand concentration} - \text{Free ligand concentration} - \text{Total ligand bound to} \ N \\
\text{Total concentration of} \ M
\]

\[
\frac{C_X - [X] - \bar{n}' C_N}{C_M} 
\]

... (78)

At the half-wave potential of the wave for the system \(N, X\) the above equation becomes

\[
\bar{n} = \frac{C_X - [X] - \bar{n}' C_N}{2C_M} 
\]

... (79)

Where:
- \(C_X\) = Total ligand concentration
- \([X]\) = Free ligand concentration
- \(\bar{n}'\) = Ligand number of the indicator system, \(N, X\)
- \(C_N\) = Concentration of indicator ion
- \(C_M\) = Concentration of the metal ion under study.

The term \(\bar{n}' C_N/2\) may be ignored since \(C_N\) is usually very much less than \(C_M\).

\[
\bar{n} = \frac{C_X - [X]}{C_M} 
\]

... (80)

Using the above equation \(\bar{n}\) can be calculated at each value of free ligand concentration. \(\bar{n}\) values plotted as a function of \(\text{log}[X]\) will give the formation curve showing the maximum coordination number for the system \(M, X\). The formation curve may be integrated graphically using Fronaeous[19] relation to give \(F_0[X]\) data as
\[ \sum_{i=1}^{N} \beta_i [X]^i = F_0 [X] = \exp \left[ \int_{0}^{[X]} \frac{1}{n} d[X] \right] \] ... (81)

or

\[ \log F_0 [X] = \int_{0}^{[X]} \log [X] \] ... (82)

The residual integral, corresponding to the lowest experimentally accessible value of [X] may be negligible but if not may be determined from the relation

\[ \lim_{[X] \rightarrow 0} F_0 [X] = \frac{1}{1 - n} \] ... (83)

Stability constants are determined from \( F_0[X] \) values using the Leden [8] extrapolation method.