PART II

CHAPTER I - Principles of Polarography
Polarography introduced by Jaroslav Heyrovsky in the early twenties is based on the characteristics of the current-voltage curves obtained when unstirred solutions of electro oxidizable or electro reducible substances are electrolysed in a cell in which one of the electrodes is a dropping mercury electrode.

When an electrolyte is subjected to electrolysis in a cell in which one of the electrodes is a dropping mercury electrode and a second non-polarizable electrode, it is plausible from the resulting current-voltage curves or polarograms to determine both the nature and concentration of the reducible or oxidizable substance or substances present.

The height of the curve is called the limiting current. This limiting current obtained with the dropping electrode is caused by a state of concentration polarization which results from the depletion of the concentration of the electrolysed substance at the electrode surface by the electrode reaction (oxidation or reduction). The current approaches the limiting plateau when the reducible or oxidizable substance is reduced or oxidized as soon as it reaches the electrode surface and its concentration at the electrode surface remains constant at a value that is negligibly small compared to that in the body of the solution. Under these conditions, the current resulting from the
The electrode reaction is independent, within certain limits of the applied e.m.f. and is governed solely by the rate of supply of the reducible or oxidizable ion to the electrode surface from the surrounding solution.

In general two forces are operating when ions are supplied to the depleted region at the electrode surface. (1) a diffusive force proportional to the concentration gradient at the electrode surface and (2) an electrical force proportional to the potential difference between the electrode surface and the solution. The limiting current can, therefore, be regarded as the sum of diffusion current and the migration current.

The current through an electrolyte solution is carried by all the ions present irrespective of whether they take part in the electrode reactions or not. The fraction of the total current carried by an ion depends mostly upon its relative concentration and to a lesser degree on its charge or in other words on the transference number of the ion. If a salt whose ions do not take part in the electrode reaction is added in excess to a solution of relatively small concentration of the reducible or oxidizable ions, the current through the solution is then transferred practically by the large excess of the added ions. Under these conditions the electrical forces on the ions taking part in the electrode reaction are practically eliminated and the limiting current becomes singularly a diffusion current.
In the case of reducible or oxidizable uncharged substances diffusion usually plays the main role in governing the limiting current because uncharged substances are not subjected to electrical migration. The indifferent salt which is added for suppressing the migration component is called the 'supporting electrolyte, base electrolyte, back ground electrolyte or carrier electrolyte'. Few salts have the complexing ability too. Some metals yield waves only in certain supporting electrolytes. These salts also give a small residual current at d.m.e. which is a sum of condenser current and the faradic current due to reducible impurities present in the solution. The magnitude of the condenser current in air-free solutions with a normal capillary and drop time is a few tenths of a micro ampere. In accurate diffusion current measurements it is essential to determine the residual current in the particular supporting electrolyte used.

The diffusion current is dependent on a number of factors including the diffusion coefficient of the depolarizing substance and its concentration in the body of the solution, the number of Faradays consumed in one mole of the electrode reaction and the area of the electrode. Polarographic measurements are mostly used to determine the concentration of the ion or the molecules in question but they are also valuable in studies of diffusion coefficients and of the products of the electrode reaction.
An important mathematical relationship pertaining to the diffusion current is shown in the Ilkovic equation:

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

where

- \( i_d \) = average diffusion current, \( \mu A \) (10^{-6} amp)
- \( n \) = number of Faradays per mole involved in the electrode reaction
- \( C \) = concentration of the electroactive material, millimoles/litre
- \( D \) = diffusion coefficient of the electroactive material, \( \text{cm}^2/\text{sec} \)
- \( a \) = rate of flow of mercury through the capillary, mg/Sec
- \( t \) = time between successive drops of mercury, Sec.

The terms \( n^{2/3} \) 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 are combined in a single factor \( I \), called the diffusion current constant given as

\[ I = 607 n D^{1/2} = \frac{i_d}{C n^{2/3} t^{1/6}} \]
The diffusion current is dependent on number of factors including the diffusion coefficient of the depolarising substance and its concentration in the body of the solution, number of faradays consumed in one mole of the electrode reaction, the area of the electrode and the transfer coefficient.

The Ilković equation is valid only if the wave obtained is solely due to diffusion of ions from the body 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 oxidised 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 the following factors are considered.

(1) $i_d$ is proportional to $a^{2/3} t^{1/6}$, when the other factors in the Ilković equation are constant. The drop time 't' depends upon the heights of mercury column. Hence, if the wave is diffusion controlled $K = i_d / \sqrt{Hg}$. 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

$$D = \frac{RT}{ZF^2 \lambda_{\infty}}$$

where,

- $R$ = the gas constant in volt-coulombs per degree
- $T$ = absolute temperature
- $\lambda_{\infty}$ = 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 per cent 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 Ilkovic equation remain constant the diffusion current $i_d$ is directly proportional
to the concentration of the reducible or oxidizable 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 allow 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 reactions.

Maxima and Maximum suppressors

Polarographic analysis is carried out with an experimental set up that ensures drop formation undisturbed by vibration or stirring. This keeps convection in a solution at minimum. However, a convection or streaming of solution results from the electrode reaction itself and is therefore very reproducible. This phenomenon exists in a thin layer around the mercury drop. Since much more material is brought to the electrode by convection than by diffusion, the currents become very much larger than pure diffusion currents. They are easily recognizable since they are not maintained over
a large voltage span but diminish more or less abruptly to the smaller value of the diffusion currents, giving rise to sharp or rounded maxima on the polarographic curves. Maxima are observed most frequently at the beginning and occasionally in the middle of the straight portion of a limiting current. A maximum may be found during a reduction or oxidation of ionised or non-ionised, organic or inorganic substances. The maxima may be acute or rounded depending on the nature and concentration of the material reduced but also on the concentration of the indifferent electrolyte and the resistance of the circuit. In general the maxima become smaller the longer the drop time of the electrode, increases with an increasing concentration of the electroactive material. Two kinds of maxima may be observed and these are maxima of the first kind and maxima of the second kind.

Maxima of both kinds are obstacle to quantitative polarographic analyses. They can be eliminated by the addition of small quantity of maximum suppressor to the solution. This substance is adsorbed on to the surface of a dropping electrode and then retards or prevents motion of the solution past the drop surface. Most popular maximum suppressors are some of the surface active reagents like gelatin, agar, organic dyes and Triton X-100. They must be
present in smaller concentration. At higher concentration they render interpretation of polarograms difficult by diminishing the limiting current of the substance itself. The effectiveness of a suppressor can be expressed as the maximum dilution or the minimum necessary for complete suppression of a given maximum.

**Application 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 oxidised 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, 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.

**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 proceed 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 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. This type of electrode reactions are known as quasi-reversible reactions. The values of standard rate constant, $k_0$, 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

\[ 0 + n e \rightleftharpoons \text{R} \quad \ldots \quad (1) \]

When the oxidised 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
\[ E = E^0 - \frac{RT}{nF} \ln \frac{a_R}{a_O} \] \quad \ldots (2)

where \( E^0 \) is the standard potential, \( a_R \) and \( a_O \) 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 \( i_d \) the diffusion current. Heyrovsky and Ilkovic derived the equation as

\[ E_{1/2} = E^0 - \frac{RT}{nF} \ln \left( \frac{D_O}{D_R} \right)^{1/2} \] \quad \ldots (3)

and

\[ E_{\text{dme}} = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d} \] \quad \ldots (4)

\[ = E_{1/2} - \frac{0.0301}{n} \log \frac{i}{i_d} \] \quad \ldots (5)

where

- \( E_{\text{dme}} \) = applied potential of the dropping mercury electrode
- \( E_{1/2} \) = half-wave potential of the depolariser
- \( i \) = mean current at the applied potential
- \( i_d \) = the diffusion current
- \( n \) = number of electrons involved in the process
- \( F \) = Faraday
The above equation indicates that a plot of
\[ \log \left( \frac{i}{i_d} - 1 \right) \text{ Vs } E \]
should give a straight line with slope equal to 0.0591/n volts which is the most common criteria 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 oxidised \( D_o \) 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
Hence for a reversible electrode reaction

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

\[ = - \frac{0.0564}{n} \quad \cdots (10) \]

The half-wave potential of a 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 oxidised form. This is the same thing as ensuring a composite wave with no inflection around the residual current curve with a solution containing both the oxidized and the reduced forms. It is worth while to make sure that the cathodic and anodic i_{d}'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 depends on the nature of the electrode reaction. For a reduction to a metal soluble in mercury dE_{1/2} / dt is about -0.7 mV/degree and for a homogeneous reduction dE_{1/2} / dt may be either positive or negative but is rarely greater than ± 1 mV/degree. The temperature coefficients 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 \( E_{1/2} \) therefore constitute a fair evidence against the reversibility of the wave.

Various methods to study reversible and irreversible electrode reactions at d.m.e. have been given in detail in succeeding sections.
Books referred


