



Theoretical Principles of Polarography

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Abstract

Polarographic method of chemical analysis was invented By Jaroslav Heyrovský in 1922. Ilkovic was the first to solve the problem of diffusion to the dropping mercury electrode in 1934. The slope of the wave is an important ingredient in the overall characteristic or classification of a polarogram. All the electrode processes can be described either as a net transfer of negative charge to the solution from the electrode-reduction, forward rate constant k_f or as a net transfer of negative charge from the solution to the electrode - oxidation, backward rate constant k_b . The use of polarography for the study of the compositions, equilibrium formation constants and dissociation constants of complexes in solution is based on the simple principles first formulated in 1935 by Heyrovsky and Ilkovic. There are two quite different types of stabilities thermodynamic stability and kinetic stability. There are two methods for estimating concentration of an electroactive species using polarographic techniques; (a) Absolute method, (b) Comparative method.

Key Words- Polarographic Maxima, Diffusion Current, Kinetics of Electrode Processes, Stability of Complex Ions in Solution, Thermodynamics.

Introduction

Polarographic method of chemical analysis was invented By Jaroslav Heyrovský¹ in 1922. Polarography is a branch of electro analytical chemistry which deal with measurement and interpretation of current-voltage curve obtained during the electrolysis of solution between two electrodes one of which is very small (i.e. polarizable electrode) Since the curve obtained with the instrument are graphical representation of the polarization of D.M.E. the apparatus was called polarograph and the records obtained with it as polarogram(Fig. 4.1).

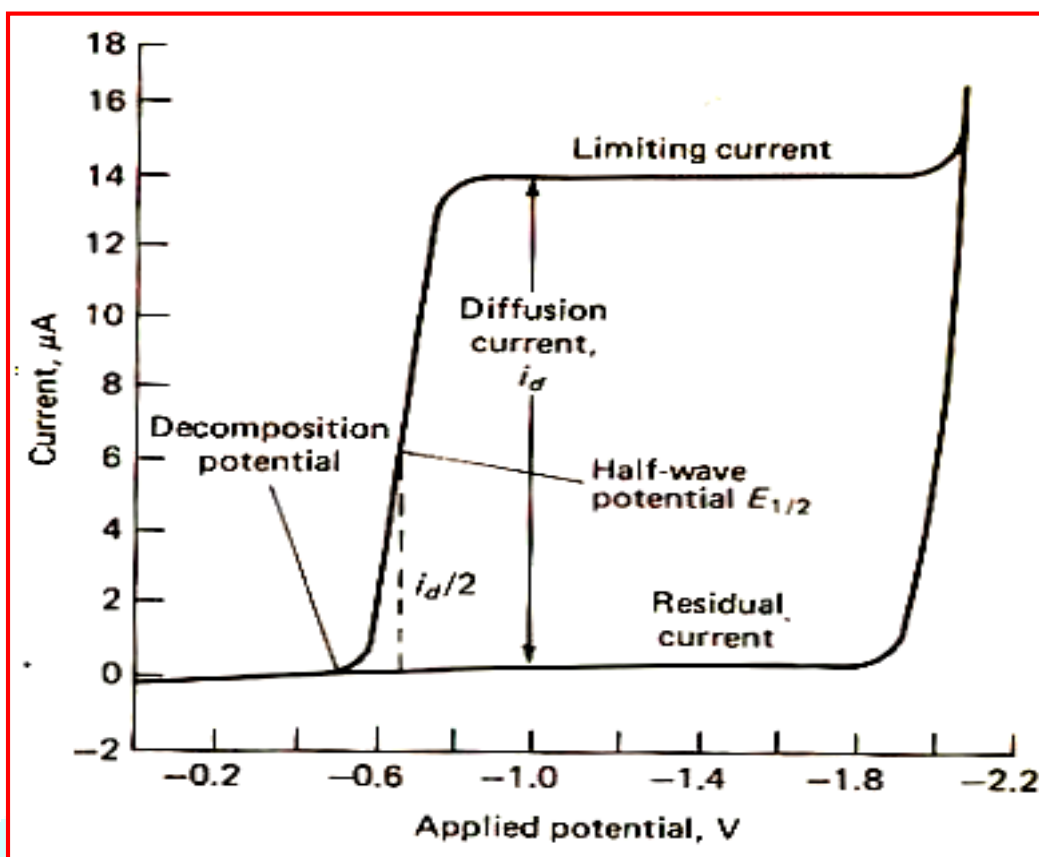


Fig. 4.1 A typical DC polarogram

During electrolysis, three modes of mass transfer to the electrodes are possible:

- (i) Migration (ii) Convection (iii) Diffusion

Migration

The migration of charged particles in electrical field is caused by the potential difference existing between the electrode surface and the solution. It can be almost eliminated if an indifferent electrolyte is added to the solution in concentration so large (normally 50 to 100 folds in excess of the electro active component of the solution) that its ions carry almost all the current. Base or Supporting electrolyte (KCl or HNO₃) is used to minimize (make it negligible) migration of electroactive species.

Convection

Movement of mass due to a natural or mechanical force is known as convection effect. Convection effects are eliminated by carrying out electrolysis in adequately controlled thermostat and by protecting the apparatus from all forms of vibrations and shocks.

Residual current

A small current is observed before the decomposition for electro reducible substance begins. This current is caused by migration and convection effect. It increases approximately directly to applied voltage. It is carried by the supporting electrolyte and impurities present in the sample.

Diffusion

It may be defined as the directed movement of substance under the influences of forces that arises from difference in concentration of the substance in various parts of the medium. This current is directly proportional to the concentration of the substance being reduced or oxidized at D.M.E. After the elimination of migration and convection effects, the diffusion becomes the sole mode of mass transfer.

THE ILKOVIC EQUATION

Ilkovic² was the first to solve the problem of diffusion to the dropping mercury electrode in 1934. The Ilkovic equation corresponds to an ideal situation, which is somewhat different from the actual conditions at the dropping mercury electrode. The current is given by the Ilkovic equation is:

$$i_d = 607 n D^{1/2} C m^{2/3} t^{1/6} \quad (4.1)$$

Where

i_d = The diffusion current in microamperes,

n = number of electrons transferred per ion,

C = concentration in millimole per litre,

D = diffusion coefficient of reducible ion in $\text{cm}^2\text{sec}^{-1}$

m = mass of mercury flowing per second in milligrams, and

t = drop time in seconds.

Lingane and Loveridge³, Strehold and Von Stackelberg⁴ obtained the following expression for the diffusion current.

$$i_d = 607 n D^{1/2} C m^{2/3} t^{1/6} \left(1 + \frac{AD^{1/2}t^{1/6}}{m^{1/3}} \right) \quad (4.2)$$

Where

$\left(1 + \frac{AD^{1/2}t^{1/6}}{m^{1/3}} \right)$ is Lingane and Loveridge correction factor for spherical electrode surface (i.e. for D.M.E.)

A = constant (the value of A is 39, according to Lingane)

THE HALF-WAVE POTENTIAL AND ITS SIGNIFICANCE

It is the potential at the middle point of a Polarographic wave where the current is equal to one half of its diffusion current. Half wave potential is generally independent of the concentration and has exact thermodynamic significance.

In case of reduction of cation to the metallic state, forming amalgam is represented as



Heyrovský and Ilkovic⁵ derived relationship between $E_{1/2}$ and potential at any point of the wave by the equation for reversible process;

$$E = E_{1/2} - (2.303RT/nF)\log(i/i_d - i) \quad (4.4)$$

Where

i = current at potential E ,

i_d = The diffusion current,

n = number of electrons transferred per ion,

F = Faraday constant,

R = Gas constant,

T = absolute temperature.

$$E = E_{1/2} - (0.0591/n)\log(i/i_d - i) \text{ at } 25^\circ\text{C} \quad (4.5)$$

A plot of E vs $\log i/(i_d - i)$ should give a straight line whose slope is equal to $0.0591/n$ volts and zero intercept on y-axis gives the value is $E_{1/2}$. In other word if $i = i_d$ than $E = E_{1/2}$. For 1 electron transfer i.e. $n = 1$, the value of slope is 59 mV, for $n=2$ its value should be 29 mV and for $n=3$ its value should be 20 mV at 25°C . This is the common criteria of thermodynamic reversibility and is also the best method for measuring $E_{1/2}$ accurately.

$E_{1/2}$ is function of the molecular form of reducible or oxidizable materials thus $E_{1/2}$ can be shifted by addition of complexing agent, varying pH, solvent composition, drop time (in irreversible systems) and nature of base electrolyte. Chemical, thermodynamic and structural information may be obtained from the measurements of the half-wave potentials of reversible and irreversible waves under varying experimental conditions.

Kirchmayer⁶ claimed that the $E_{1/2}$ of the reduction of a metal ion to metallic state depends on the structure of amalgam formed; while Vandenberg and Sellers⁷⁻⁹ studied the effect of supporting electrolyte concerning with effect of adsorption of the component of a reactant takes place at the electrode.

Dependence of dielectric constant of the medium over potential has been studied by Amis¹⁰. Butler and Kaye¹¹ have studied the effect of absence of excess of complexing agent on the polarographic wave in the reduction of complexed ions, while Koryta¹² calculated the necessary excess of ligand that is required for particular case. Hale¹³ has reviewed the literature on the determination of stability constants of complexes followed by Irving¹⁴, Crow¹⁵, Sundaram¹⁶, Reita Tamamushi and Sato¹⁷. Zahradnik and Parkanyi¹⁸ studied correlation of polarographic half-wave potentials with quantum chemical characteristics. Zuman¹⁹⁻²¹ studied the effects of various substituents and other parameters on $E_{1/2}$ of organic compounds in detail.

POLAROGRAPHIC MAXIMA

In some instances an increase of current is observed on polarographic curves followed by a decrease until at sufficiently negative potentials, the value of limitation current is reached. This shape of current voltage curve is termed as maxima.

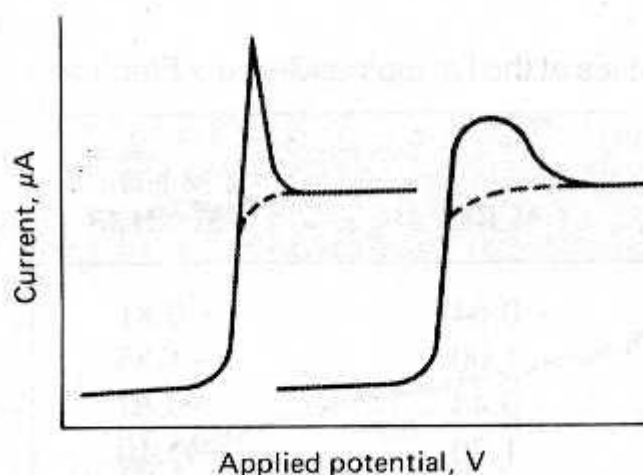


Fig. 4.2 The Polarographic Maxima

Polarographic maxima are caused by the tangential motion of the interface mercury—electrolyte. This is caused by increased transport of the depolarizer towards the electrode by a streaming motion of the solution. Such maxima are reproducible and called streaming maxima²²⁻²³. According to their occurrence and properties, they are divided into maxima of the first and of the second kinds.

Maxima of First kind

In this stirring is caused by a gradient of interfacial tension at the surface of DME. "Pure" maxima of the first kind are observed in dilute solutions of supporting electrolyte. Maxima of the first kind, appearing on the rising portion of the polarographic curves.

Maxima of Second Kind

In this stirring is caused by the flow of mercury out of the capillary²⁴. Typical maxima of the 2nd kind require rather high concentrations of supporting electrolyte and at high mercury flow rate, are usually rounded and do not fall discontinuously to the limiting current as do maxima of the first kind. Current in maxima of second kind does not fall back abruptly to limiting current and it decreases slowly. Maxima of the second kind may be suppressed by reducing the flow rate, e.g. by lowering the height of the mercury head.

Frumkin and Levich²⁵ gave a satisfactory semi quantitative interpretation of the whole group of these phenomena. This interpretation is based on such well-known concepts of electrochemistry and mechanics as interfacial tension, diffuse double-layer theory and the theory of motion of fluids.

In general, the polarographic maxima do not supply new data on electrode processes or properties of the interface and may thus be considered as an unwelcome parasitic phenomenon. This can be practically removed by addition of few drops of Triton X-100 or gelatin.

REVERSIBLE AND IRREVERSIBLE NATURE OF POLAROGRAPHIC WAVE

The slope of the wave is an important ingredient in the overall characteristic or classification of a polarogram. (Fig. 2.3)

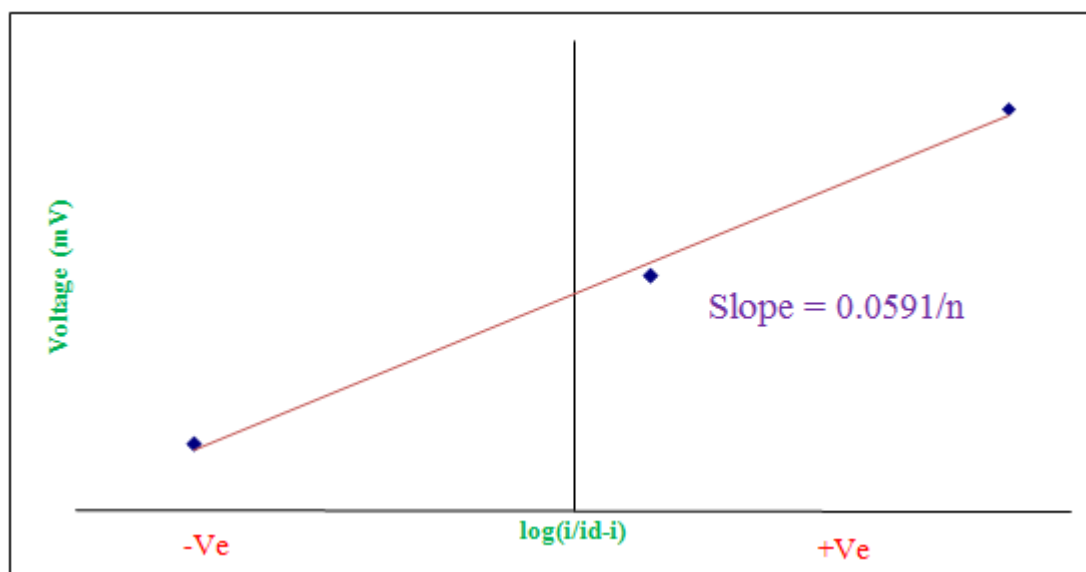


Fig. 2.3 plot E vs. $\log(i/i_d-i)$ at 25°C.

In reversible system, the linear plot of E vs $\log [i/(i_d-i)]$ has a slope $0.0591/n$, in addition to this, the $E_{1/2}$ is independent of concentration of the depolarizer and the drop time. At the same time the $E_{1/2}(\text{ox}) = E_{1/2}(\text{red.}) = E^\circ$, i.e. the half-wave potential of the oxidized and reduced form are identical and equal to the standard potential measured by equilibrium method (e.g. potentiometry). Then and then only the system will be 'Reversible' assuming that both the processes are fast.

The slope of irreversible wave will be $0.0591/\alpha n$, where α (transfer coefficient) < 1 . In irreversible system, proposed product gives a wave at potential, different from that of the wave of depolarizer.

A quantitative treatment of current potential curves has been given by Randles²⁶ and Sevcik²⁷ for reversible processes and by Delahay²⁸⁻²⁹ for irreversible processes.

KINETICS OF ELECTRODE PROCESSES

All the electrode processes can be described either as a net transfer of negative charge to the solution from the electrode-reduction, forward rate constant k_f or as a net transfer of negative charge from the solution to the electrode - oxidation, backward rate constant k_b . The rate constant k_f and k_b are the overall heterogeneous rate constants of the transitions.



The concept that a substance, which undergoes a chemical transformation, has to overcome an energy barrier is applicable to any type of reaction, but for an electrochemical reaction, the effect of the electric field has to be taken into account.

The difference between the half-wave potential of the irreversible wave and the standard potential E° (virtually equal to the $E_{1/2}$ of a reversible wave) is the polarographic over-potential (over voltage) $\eta_{1/2}$.

$$\eta_{1/2} = (E_{1/2})_{\text{irrev.}} - E^\circ \quad (4.7)$$

Thus an electrochemical reaction without considerable over voltage is termed as reversible reaction. The slope of an irreversible wave differs from the thermodynamic value calculated from the equation for a reversible wave; the E vs. $\log i/i_d - i$ plot, is often linear but the number of electrons determined from its slope is smaller than that of the actual number of electrons consumed in the electrode process. The slow establishment of equilibrium between the oxidized and reduced form at the electrode surface i.e. a slow electrode process, is regarded as the cause of irreversibility. The electrode process in this sense refers only to electron exchange between the depolarizer and the electrode and not to the mass transfer towards the electrode. If this is to be included, the term overall electrode process or depolarization process is used.

The general equation for a polarographic wave corresponding to the reduction of the oxidized form of the redox system is given by the expression:

$$(i_d - i)/i = \exp [nF(E - E^\circ)/RT] + (1.14/k_s) \sqrt{D/t} \exp[\alpha nF(E - E^\circ)/RT] \quad (4.8)$$

Where k_s = standard rate constant,
 k_f° = rate constants at $E = 0$ and
 α = transfer coefficient.

Two limiting cases arise according to value k_s . If k_s is sufficiently high so that the expression $k_s \sqrt{D/t} \gg 1$ the second right hand side term in equation (4.8) can be neglected and the Heyrovsky Ilkovic equation is obtained:

$$(i_d - i)/i = \exp[nF(E - E^\circ)/RT] \quad (4.9)$$

This expresses the shape of the polarographic curves corresponding to the reversible electrode. In this case $E_{1/2}$ differs from the standard redox potential E° of a true redox system (both forms in the solution) only by the term $(RT/nF) \ln \sqrt{D_{\text{ox}} / D_{\text{red}}}$ which is, in most cases, negligible.

On the other side, if the rate constant k_s is lower than about $2 \times 10^{-2} \text{ cm sec}^{-1}$, the second right hand term of the above equation is no longer negligible and the half wave potential is considerably shifted to more negative value. Such electrode processes are called irreversible.

The theory of irreversible waves was first developed by Eyring and coworkers³⁰ and Tanaka and Tamamushi³¹, but a more rigorous treatment was made by several workers³²⁻³³. Irreversible waves were further classified into two classes depending upon the k_s values (i) If rate constant lies within $2 \times 10^{-2} > k_s > 5 \times 10^{-5} \text{ cm sec}^{-1}$, the reaction is called quasi reversible, and if $k_s \leq 5 \times 10^{-5} \text{ cm sec}^{-1}$ the process is totally irreversible.

Studies were made by Koryta³⁴, Matsuda³⁵⁻³⁶ and Gellings³⁷. Matsuda determined $E_{1/2}^f$ (half wave potential for reversible reduction of irreversible wave) while Gellings applied famous Langrange's theorem to determine $E_{1/2}^f$ and other parameters. These methods were successfully applied by Tamamushi, Ishibashi and Tanaka³⁸ who compared various results obtained. Tanaka

and Tamamushi³⁹ gave excellent critical views in their review, in which they compared various results obtained by different methods.

Meites and Israel⁴⁰ extended Koutecky's method for irreversible waves and gave a mathematical form in place of graphical representation. In our department Gaur and Bhargava⁴¹ extended Koutecky's treatment for irreversible waves by considering spherical diffusion of mercury drops in place of linear diffusion. Sundaram and Saraiya⁴² have presented one more review.

KOUTECKY'S METHOD

Koutecky, first of all gave the treatment for the electrode reactions of the dropping mercury electrode, controlled by the kinetics of electron transfer. The mathematical solution for such electrode reactions at the dropping mercury electrode is given by

$$i_i/i_d = F(X) - \xi \bar{H}_c(X) = \bar{F}(X) \quad (4.10)$$

where

$$X = k_f(12t/7D)^{1/2} \text{ and } \xi = 50.4 D^{1/2} m^{-1/3} t^{1/6}$$

i_i is the maximum instantaneous current of the single drop at the potential E, i_d is the maximum instantaneous current of the single drop in the limiting current region, t is the drop time in the limiting current region and D, the diffusion coefficient, (X) is a function relating the current at potential E to the current at infinity and is given by³²

$$i/i_\infty = (\partial C / \partial S_1) \sqrt{\pi/2} = \sqrt{\pi/2} \sum_{i=1}^{\infty} r_i X^i = \bar{F}(X) \quad (4.11)$$

$$\text{and } H_c(X) = (0.7868F(X)) \sqrt{\pi/2} \sum_{i=1}^{\infty} r_i X^i \quad (4.12)$$

where $H_c(X)$ is the correction factor introduced because of the curvature of the drop. The numerical values of $F(X)$ and $H_c(X)$ have been taken from Koutecky's original papers. k_f is the rate constant for the forward reaction in the irreversible process which varies with the electrode potential E according to relation-

$$k_f = k_f^\circ \exp(-\alpha nFE/RT) \quad (4.13)$$

where α is the transfer coefficient, n is the number of electrons involved in the rate determining step and k_f° is the rate constant of the electron transfer at zero volt (N.H.E.).

The plot of $-\log k_f$ vs E (N.H.E.) gives a straight line, the slope of which is equal to $\alpha nF/2.303RT$ from which αn values can be calculated. The extrapolation to the values of E° (standard electrode potential) to zero volt, gave the values of k_s and k_f° respectively.

MODIFICATION OF KOUTECKY'S METHOD

(I) Meites and Israel's Modification

Meites and Israel⁴⁰ have extended the method of Koutecky into a more mathematical form. They found that $\log X$ varies linearly with $\log F(x)/\{1-F(x)\}$. The plot of $-\log k_f$ vs E (N.H.E.) gives a straight line, the slope of which is equal to $\alpha n F/2.303RT$ from which αn values can be calculated. The extrapolation to the values of E° (standard electrode potential) to zero volt gives the values of k_s and k_f° respectively.

$$\log \lambda = -0.1300 + 0.9163 \log F(x)/\{1-F(x)\} \quad (4.14)$$

where for simplicity they have taken $\lambda = (7/12)^{1/2}x$ and they assume that diffusion at the electrode surface is linear. Then equation (4.10) is virtually equals to $F(x)$ so equation (4.14) can be written as

$$\log \lambda = -0.1300 + 0.9163 \log \frac{i}{i_d - i} \quad (4.15)$$

The heterogeneous rate constant can be described by

$$k_{f,h} = k_{fh}^0 \exp\left[\frac{-\alpha n F E}{RT}\right] \quad (4.16)$$

The combination of equations (4.9), (4.15) and (4.16) yields the result

$$E_{d.e.} = \frac{0.05915}{\alpha n} \log \frac{1.349 k_{fh}^0 t^{1/2}}{D^{1/2}} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i} \quad (4.17)$$

which may be written as

$$E_{d.e.} = E_{1/2} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i} \quad (4.18)$$

with

$$E_{1/2} = \frac{0.05915}{\alpha n} \log \frac{1.349 k_{fh}^0 t^{1/2}}{D^{1/2}} \quad (4.19)$$

in these equations both $E_{d.e.}$ and $E_{1/2}$ are referred to N.H.E.

(II) Gaur and Bhargava's Modification

Gaur and Bhargava have extended the Koutecky's treatment for irreversible waves. Instead of equation (4.13), Gaur and Bhargava⁴¹ have found

$$\log \lambda = 0.0523 + 0.9619 \log \frac{i}{i_d - i} \quad (4.20)$$

On combining equations (4.11) (4.16) and (4.20), they obtained

$$E_{d.e.} = \frac{0.05915}{\alpha n} \log \frac{k_{fh}^{\circ} t^{1/2}}{1.128 \times D^{1/2}} - \frac{0.05690}{\alpha n} \log \frac{i}{i_d - i} \quad (4.21)$$

which may be written as

$$E_{d.e.} = E_{1/2} - \frac{0.05690}{\alpha n} \log \frac{i}{i_d - i}$$

with

$$E_{1/2} = \frac{0.05915}{\alpha n} \log \frac{k_{fh}^{\circ} t^{1/2}}{1.128 \times D^{1/2}} \quad (4.22)$$

In deriving equation (4.15) and (4.20), Gaur et al. considered that the diffusion to the electrode surface is linear, but if the spherical diffusion was considered, then the second factor of equations (4.10) i.e. $\xi Hc(X)$. The values of ξ were considered between 0.0 and 0.3 and corresponding $F'(x)$ values were determined. It was found that $\log X$ again varied linearly with $\log F'X/\{(1-F'(x))\}$.

For all values of ξ , it was shown that

$$\text{Log } \lambda = c + m \log F'(x)/\{1\xi-F'(x)\} \quad (4.23)$$

linear relationship between x and c was found to be

$$c = 0.0523 + 0.3335\xi \quad (4.24)$$

Values of m also increase with the increase in value of ξ when it is below 0.1, then onwards it becomes constant.

On combining equation (4.11), (4.16) and (4.23), it was found that

$$E_{d.e.} = \frac{0.05915}{\alpha n} \log \frac{k_{fh}^{\circ} t^{1/2}}{(\text{antilog } c)D^{1/2}} - \frac{0.05915}{\alpha n} \log \frac{i}{i_d - i} \quad (4.25)$$

which may be written as

$$E_{d.e.} = E_{1/2} - \frac{0.05915}{\alpha n} \log \frac{i}{i_d - i}$$

with

$$E_{1/2} = \frac{0.05915}{\alpha n} \log \frac{k_{fh}^{\circ} t^{1/2}}{(\text{antilog } c)D^{1/2}} \quad (4.26)$$

In equation (4.19), (4.20) and (4.26), potentials are referred to N.H.E. If potentials are referred to standard potential of that couple, then the equation will correspond to the standard rate constant.

STABILITY OF COMPLEX IONS IN SOLUTION

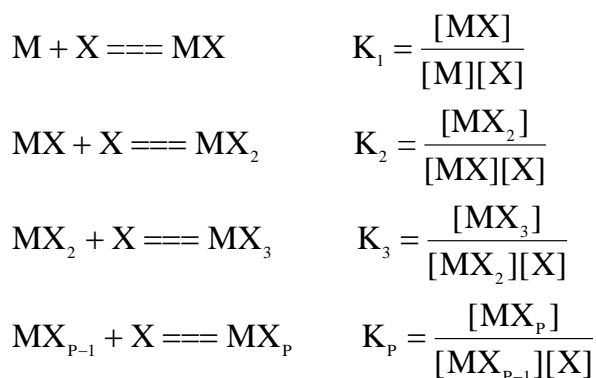
The use of polarography for the study of the compositions, equilibrium formation constants, and dissociation constants of complexes in solution is based on the simple principles first formulated in 1935 by Heyrovsky and Ilkovic⁵. The electrode reduction or oxidation of any depolariser at a mercury electrode is reflected in the polarogram by the corresponding wave whose principal parameters are the half-wave potential $E_{1/2}$ and the limiting current i_d .

The direction and magnitude of the shift of the wave depend on which component of the redox system forms a more stable complex, the composition of the complex, and its equilibrium formation constant. Polarography makes it possible to obtain information not only about the equilibrium properties of the complexes but also about the mechanisms and kinetics of electrode processes involving them, the kinetics of the dissociation of the complexes, and their electrochemical activity as a function of structures.

In the course of the study of equilibria in solutions by the polarographic method, instances of simple and stepwise complex formation, the formation of mixed-ligand and polynuclear complexes, the formation of complexes by metal ions with ligands involved in complex acid–base interactions and the formation of molecular organic complexes and ion pairs have been examined. Methods of calculation from experimental data, including computer calculations, have been greatly improved and methods have been proposed for the investigation of electrochemically inactive complexes with the aid of indicator ions; it has become possible to use kinetic and catalytic waves as well as waves due to irreversible processes. One may conclude that, the level of development of the polarographic method in this field is high⁴³⁻⁴⁷.

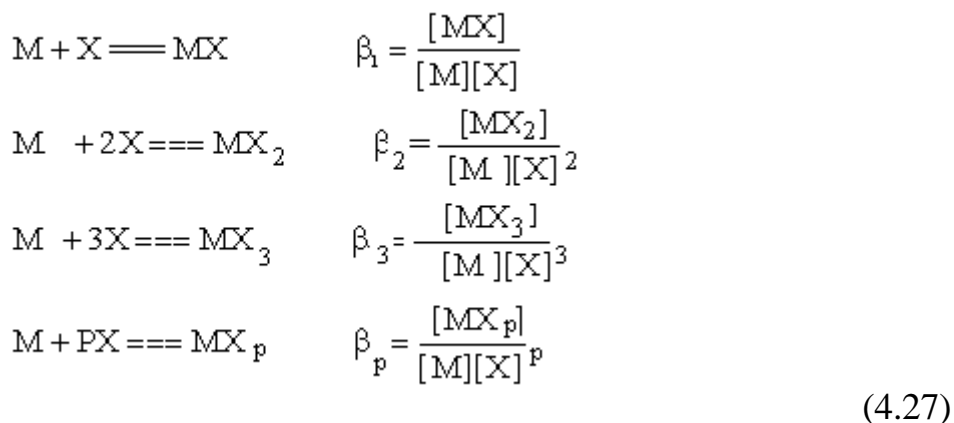
In order to determine the formation of coordination complexes in solution, two kinds of stability comes into question, namely thermodynamic stability and kinetic stability. The thermodynamic stability of a species is a measure of the extent to which this species will form or be transformed into other species under certain conditions when the system has reached equilibrium. The kinetic stability of a species refers to the speed with which transformation leading to the attainment of equilibrium will occur.

Let us consider problems of thermodynamic stability. Bjerrum⁴⁸ was the first to establish that the function of a complex species MX_p in solutions must proceed through a series of intermediate stages.



There will be ‘P’ such equilibria, where ‘P’ represents the maximum coordination number of the metal ion M for the ligand X, ‘P’ may vary from one ligand to another.

Alternatively, equilibrium relation can also be expressed as follows:



Since there can be only 'P' independent equilibrium in such a system, hence obviously K's and β 's must be related. On multiplying the numerator and denominator of the expression for β_3 by [MX] and [MX₂] and on subsequent rearrangement, we obtain

$$\beta_3 = K_1 \cdot K_2 \cdot K_3 \tag{4.28}$$

generalizing the above equation, we obtain the following generalized relation,

$$\beta_K = K_1 \cdot K_2 \cdot K_3 \dots \dots \dots K_K \tag{4.29}$$

The K's are called the stepwise formation constants or stepwise stability constants, while β 's are called the overall formation constants or overall stability constants.

REVERSIBLE ELECTRODE PROCESSES INVOLVING COMPLEXES

Reversible electrode processes involving complexes are more favourable for the study of the compositions of the complexes and their equilibrium formation constants, because it is possible to derive definite useful relations even for very complex systems.

In a system with complex formation a series of species are present simultaneously at equilibrium: free metal ions, complex species of various compositions, and the free ligand. In principle, not only free metal ions are discharged at the electrode, which is usually assumed for simplicity in the derivation of the equations, but also the complex species.

Formation of a Simple Complex

The very first method to determine the stability and coordination number of the complex was suggested by Lingane⁴⁹ and he gave the following expression,

$$(E_{1/2})_s - (E_{1/2})_c = \frac{0.05918}{n} \log \beta_j + j \frac{0.059158}{n} \log C_x \tag{4.30}$$

(at 25°C)

in which (E_{1/2})_s and (E_{1/2})_c are the half wave potential of the simple and complexed species, respectively, j is the coordination number of the complex, β_j is its stability constants and C_x the ligand concentration. E_{1/2} of the complex metal ions shifts with changing activity of the complexing ligand in accordance with

$$\frac{\Delta E_{1/2}}{\Delta \log C_x f_x} = -j \frac{0.05918}{n} \text{ (at } 25^\circ \text{C)} \quad (4.31)$$

Hence the number of ligands, j , bound in the complex is found from the plot of $\log C_x$ against $(E)_c$, which in the present case, should be linear. However, this method had limited scope, as it was useful only for those systems in which one complex species is formed. This method could be extended to some peculiar case, where the curve between $E_{1/2}$ and $-\log C_x$ is a segmented curve.

METHOD OF DEFORD AND HUME

The presence of successively formed complex species is indicated if a plot of $(E_{1/2})$ vs $-\log C_x$ appears as a smooth curve. De-Ford and Hume⁵⁰ have derived a method for evaluating the consecutive stability constants of such systems. According to them, the function $F_0(x)$ may be expressed in the form-

$$F_0(x) = \text{antilog} \left[0.4343 \frac{nF}{RT} \{ (E_{1/2})_s - (E_{1/2})_c \} \right] + \log \frac{I_m}{I_c} \quad (4.32)$$

$$F_0(x) = \text{antilog} \left[0.4343 \frac{nF}{RT} \Delta E_{1/2} \right] + \log \frac{I_m}{I_c} \quad (4.33)$$

Crow⁵¹ and Irving⁵² have used the symbol $F_0[X]$ in place of $F_0(x)$ to emphasize that it is a function of the free ligand concentration.

This relation may be expressed in the form:

$$F_0(x) = \beta_0 + \beta_1[X] + \beta_2[X]^2 + \dots \dots \dots \beta_N[X]^N \quad (4.34)$$

Here β_0 is the stability constant of zero order complex, which by definition has the value of 1 (unity).

The different values of $F_0(x)$ are obtained at variable concentration of ligand which are very high in comparison to the concentration of the metal ion. The plot of $F_0(x)$ vs $[Cx]$ gives a steeply rising curve. The intercept on $F_0(x)$ at $x = 0$, is unity and the slope is β_1 .

Now a new function $F_1[X]$ is given by

$$F_1(X) = \frac{F_0[X] - 1}{[X]} = \beta_1 + \beta_2[X] + \dots \dots \dots + \beta_N[X]^{N-1} \quad (4.35)$$

in similar way other functions are also introduced:

$$F_2(X) = \frac{F_1[X] - \beta_1}{[X]} = \beta_2 + \beta_3[X] + \dots \dots \dots + \beta_N[X]^{N-2}$$

$$F_3(X) = \frac{F_2[X] - \beta_2}{[X]} = \beta_3 + \beta_N[X] + \dots \dots \dots + \beta_N[X]^{N-3}$$

$$F_N(X) = \frac{F_{N-1}[X] - \beta_{N-1}}{[X]} = \beta_N$$

The plot of $F_1[x]$ vs $[x]$ gives an intercept of β_1 on $F_1[x]$ axis and slope of β_2 as $[X]$ approaches zero. In this way confirmation of β_1 value is done.

For the last but one complex a straight line will be obtained with an intercept of β_{N-1} and slope of β_N . A parallel line to X-axis with an intercept of β_N will be obtained for the highest complex species.

It must be noted that in our derivation, activity coefficient terms have been ignored. It is convenient to keep activity coefficient terms constant (so that these cancel out) rather than attempting their approximate calculation by tedious methods. This is achieved by holding the ionic strength constant for each system. These stability constants are not the true thermodynamic values but hold good only in the media of same ionic strength. The condition is more favourable if the ligand is an uncharged molecule.

Other Methods

Many other theoretical treatments are also available to study metal complex by polarography such as D. R. Crow method⁵³⁻⁵⁴, Schwarzenbach⁵⁵ etc.

IRREVERSIBLE ELECTRODE PROCESSES INVOLVING COMPLEXES

Several approaches, permitting the study of the equilibrium properties of complexes which are reduced irreversibly at the dropping mercury electrode, have been developed.

1. Determination of the Characteristics of the Complex from the Shift of the Half-Wave Potential

The principles of the study of the equilibria in the formation of complexes under conditions where the reduction is fully irreversible have been examined in detail⁵⁶. Equation have been derived for the current at any point in the polarographic wave and for the half-wave potential under the following conditions: (1) only mononuclear complexes are formed in solution; (2) the complex formation is rapid; (3) each complex can be reduced at the electrode independently with formation of an amalgam; (4) there is no specific adsorption in the experimental range of potentials.

2. The Study of Complex Formation on the Basis of Limiting Diffusion Currents

The limiting diffusion current is the second source of information about complex formation in classical polarography. In fact, complex formation leads to a significant change in the size of the species; one must then bear in mind not only the dimensions of the central ions and the ligands but also those of the solvation shell around the complex species. This alters the diffusion coefficient of the species. The dependence of the limiting current on the ligand concentration is frequently of the expected type and can be used to determine the stability constants of the complexes⁵⁷⁻⁵⁸.

The use of limiting diffusion currents for the calculation of equilibrium constants has an advantage over methods based on the measurement of half-wave potentials, which consists in

the fact that it is applicable to all processes regardless of their reversibility. Instances of the successful application of this method in the study of the equilibria in the formation of ionic associated species have been described in a review¹⁷.

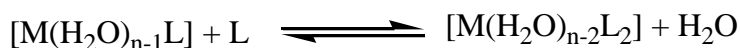
3. The Indicator Method

An indicator method has been proposed⁵⁹ for the determination of the stability constants, which is suitable when the complex is reduced irreversibly or is altogether electrochemically inactive. Its essential feature is as follows. One selects an indicator ion whose complexes with the given ligand are reduced reversibly and at less negative potentials than the complex investigated. The dependence of $E_{1/2}$ for the indicator ion on the ligand concentration is plotted on the basis of experimental or calculated (if the stability constants are known) data, and then the test cation is introduced into the solution and the change in $E_{1/2}$ for the indicator ion, occurring as a result of the formation of a complex by the test ion with the given ligand, is measured.

Thermodynamics

There are two quite different types of stabilities thermodynamic stability and kinetic stability. When we are concerned with former, we deal with metal ligand bond energies, stability constants and several thermodynamic variables which are derived from them. When we are interested in kinetic stability of formed complexes then we deal with the rate and mechanism of chemical reactions (substitution, isomerization, racemization and electron or group transfer reactions) as well as with the thermodynamic variables involved in the formation of intermediate species or activated complexes. In the kinetic sense it will be more proper to speak of complexes as being inert or labile rather than stable or unstable. Thus a thermodynamically stable complex may be labile or it may be inert. For example we find that $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$ have roughly same energy per bond 116 and 122 Kcal /mole respectively but the former is labile and exchanges its ligands very rapidly while the later is inert and exchanges its ligand very slowly ($t_{1/2} \sim 3.5 \times 10^5$ sec.).

We may make a satisfactory approximation to the desired information by an alternative but measurable path. Thus we can study formation constants for complex ions in solution where, for example the reaction in aqueous medium may be represented as follows:-

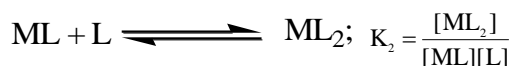


or overall

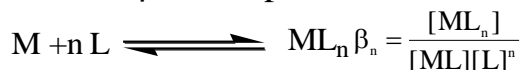


for each of the forgoing equilibria, we can write an equilibria constant expression in accordance with the law of mass action. Omitting the solvent water, whose activity does not change if low concentrations are assumed, we obtain the following expressions.





where the constants $K_1, K_2, K_n \dots$ are called the stepwise stability or formation constants and the bracketed quantities represent the activities of the enclosed species. The overall formation constant β , is the product of the successive formation constants.



$$\beta_n = K_1 K_2 \dots K_n = \sum_{i=1}^{i=n} K_i$$

and it is this value that is used to determine the thermodynamic functions. The standard free energy change ΔF° (or ΔG°) is related to the equilibrium constant, β by the relation

$$\Delta G^\circ = -2.303 RT \log \beta$$

By measuring β at two temperatures we may obtain ΔH° by equation

$$\Delta H^\circ = - \frac{2.303RT_1T_2 \left[\log \frac{\beta_{T_1}}{\beta_{T_2}} \right]}{T_2 - T_1} \quad (4.42)$$

and we know that

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\text{or } 2.303RT \log \beta = T\Delta S^\circ - \Delta H^\circ \quad (4.43)$$

From the above equation (4.43) it is obvious that complex formation is favoured by negative enthalpy changes and positive entropy changes. In many instances both changes are found to favour complex formation but there are also many complexes where only one of these quantities is favourable. From the stepwise formation constant we may obtain stepwise enthalpy changes. In aqueous solutions these have values in the range +5 to -5 Kcal/mole for ionic ligand, 0 to -5 Kcal/mole for neutral ligand and for multidentate the value may run over -20 Kcal/mole.

Generally the higher the charge and the greater the number of donor atoms to the chelating ligand the larger will be entropy increase.

Further, as it is the concern of thermodynamics of irreversible systems, different equations have been followed to evaluate thermodynamic parameters.

The enthalpy of activation at constant pressure (ΔH_p^\ddagger) has been calculated by substituting the value of slope of the plot ($\log k^\circ_{fh}$ vs $-1/T$) in the Vant Hoff equation⁵⁴. Where k°_{fh} is the formal forward rate constant.

$$\Delta H_p^\ddagger = 2.303 R \text{ slope} \quad (4.44)$$

R = Gas constant

$$\Delta H_p^\ddagger = \Delta H_v^\ddagger + RT \quad (4.45)$$

From this relation $\Delta H_v^\#$ (Enthalpy of activation at constant volume) has been evaluated.

Where K is the Boltzmann constant, h is the Plank's constant, r_0 is mean distance between depolarized ions in the bulk solution, R is gas constant, T is the absolute temperature. In general value of r_0 is taken as $2 \times 10^{-8} \text{ cm}^{60}$.

Positive value of $\Delta G^\#$ suggests non spontaneous nature of electrode process and negative value of $\Delta G^\#$ suggests spontaneous nature of electrode process⁶¹. Similarly positive value of $\Delta S^\#$ suggests that formation of activated state is accompanied by increase of entropy.

INTERPRETATION OF THE WAVE HEIGHT

There are two methods for estimating concentration of an electroactive species using polarographic techniques; (a) Absolute method, (b) Comparative method.

Absolute method is based on the use of the diffusion current constant. Its characteristic is that different capillaries are used with the unknown and known solutions, and so it involves the errors inherent in the equations describing the relationship between the wave height and the capillary characteristics. Hence it is appreciably less accurate than the comparative method, in which the calibration data are obtained with the same capillary and same condition used to analyze unknowns.

There are four principal comparative methods, which are discussed below in approximately their order of increasing complexity.

1. The Standard Addition Method
2. The Standard Curve Method
3. The Standard Sample Method
4. Pilot Ion Method or Internal Standard Method.

We have used the standard addition method for analysis.

1. The Standard Addition Method

The method of standard addition, which appears to have been originated by Hohn, is most widely used for quantitative estimation of an electroactive species⁶². There are three standard addition method, all based on the increase of wave height produced by adding a known amount of the substance being determined.

In the commonest the polarogram of the unknown solution is first recorded, and then a known volume of a standard solution of the substance of interest is added to the unknown solution and a second polarogram is recorded. From the increase in current value caused by the known addition, concentration of unknown solution can be computed; using the formula.

$$C_u = \frac{i_1 v C_s}{i_2 v + (i_2 - i_1)V} \quad (4.46)$$

Where

C_u = Concentration of the unknown solution

i_1 = Wave height of the unknown solution

C_s = Concentration of the standard solution

v = Volume of the standard solution added

V = Volume of the sample solution taken

i_2 = Wave height of the solution after adding known amount of the Standard solution.

The size of addition is important as it influences the relative error of the results. According to Reinmuth⁶³ optimum precision is usually obtained if the concentration is equal to C_{max} (the upper limit of concentration above which wave height of a substance is no longer proportional to its concentrations) after the standard addition and if the standard addition roughly doubles the concentration, for this minimize both the uncertainty in i_1 - i_2 and the uncertainty contributed by the correction of i_1 and i_2 for residual current. If C_u is considered to be fixed, the best result is obtained if the standard addition is large though it must not be so large⁶⁴ that C_{max} is exceeded.

In another standard method (standard spike method), two identical samples of the unknown are weighed out and a known weight of the substance being determined is added to one of them. Both the solutions are diluted to the same volume and their polarograms are recorded under identical condition. If W_u is the weight of the substance being determined in the "unspiked" sample (one in which we haven't added any standard solution) and weight added to the other sample is W_s .

$$W_u = \frac{W_s i_1}{i_2 - i_1}$$

This is a more time consuming method. However, its advantage is that it eliminates uncertainties caused by dilution accompanying the standard addition.

The third kind of standard addition method, called double standard addition method, has two uses. One is to provide an approach to the wave separation problem and another is to compensate the changes in the diffusion current constant of the substance being determined. In this form, the concentration of the unknown solution is determined using an expression.

$$C_u = \frac{i_2(V + v_1 + v_2)(v_1+v_2) - i_3v_1(V + v_1)}{i_3(V + v_1) - i_2(V+v_1+v_2)} \times \frac{C_s}{V} \quad (4.48)$$

Where,

$V =$ Volume of the solution taken

$C_u =$ Concentration of the unknown solution

$v_1 =$ Volume of the standard solution added to the unknown solution.

$i_2 =$ Wave height of the solution after first addition

$v_2 =$ Volume of the standard solution added second time to the unknown Solution

$i_3 =$ Wave height of the solution after second addition.

2. The Standard Curve Method

In this method, polarograms of a number of solutions containing known amounts of the electro-active species of interest are recorded and their wave heights are measured. These data are used to construct a standard curve i.e. then used to obtain the concentration of unknown solutions from their wave heights⁶⁵⁻⁶⁶. The polarograms of known and unknown must be secured under exactly identical experimental conditions.

3. The Standard Sample Method

It includes the measurement of wave heights of a standard sample at the same time that the unknown is analyzed⁶⁷. Comparison of the two wave heights directly gives the concentration of the unknown solution.

$$\frac{i_{d1}}{C_1} = \frac{i_{d2}}{C_2} \quad (4.49)$$

Where,

$i_{d1} =$ diffusion current of the standard sample solution

$i_{d2} =$ diffusion current of the unknown solution

$C_1 =$ concentration of the standard sample solution

$C_2 =$ concentration of the unknown solution

4. Pilot Ion Method or Internal Standard Method

The Pilot Ion method, sometime called “quotient of two waves” method⁶⁸, depends on the fact that the ratio of the heights of two diffusion controlled waves is particularly independent of such experimental variables as the temperature, the capillary characteristic, and the concentration and viscosity of the supporting electrolyte.

This method permits the determination of several substances from the polarogram of single solution containing a known amount or concentration of one pilot ion. The pilot-ion method is uniquely advantageous in rapid routine analysis because its compensation for variations of the experimental conditions is so perfect that quite accurate results can be obtained very rapidly.

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