CHAPTER - II

ELECTROANALYTICAL TECHNIQUES

2.1 GENERAL INTRODUCTION

An electroanalytical technique may be defined as an analytical method in which measurement of one or more electrical properties is used either directly to calculate the concentration of a substance in solution or indirectly to locate an equivalence point. The fundamental properties are current, potential and resistance. Based on the measurement of these parameters, different electroanalytical techniques have been developed.

Electroanalytical methods may also be divided into two groups; the steady state methods and the non-steady state methods. In the steady state methods the measurements are made only after the steady state is reached that is the current potential relationship is independent of time. The non-steady state methods are based on current-potential-time relationship. Such non-steady state methods have further been divided into two groups depending upon whether the electrode potential is controlled or the cell current is controlled. When the electrolysis is studied by keeping the electrode potential constant and observing the variation of current with time, the method is known as chronoamperometry, whereas in the other process known as chronopotentiometry the electrolysis current is kept constant and the variation of potential is measured as a function of time.

An electrochemical reaction occurring at an electrode surface described as $O + n e \rightleftharpoons R$ involves the following steps.

1. Mass transfer of the reductant or oxidant to the vicinity of the electrode surface.
2. The occurence of a chemical reaction in the electrochemical double layer to give species that participates in the actual electron transfer process.
3. The actual electron transfer process.
4. The structural reorganisation and chemical reaction of the intermediate product of the charge transfer process to give a species that is stable either in solution or on the electrode surface.
5. The removal of final product of the charge transfer process either by mass transfer to the bulk of solution or by deposition on the electrode surface.

The electroanalytical techniques are mainly employed for studying the electrode kinetics and for quantitative determination of an electroactive substance. One of the most important of such techniques is voltammetry.

Voltammetry is an electroanalytical technique where a controlled variable potential is applied to a working electrode, usually a microelectrode and the variation in current

as a function of applied potential is the measured quantity.

The applied potential E is given by

$$E = E_i + \gamma t \qquad 2.1$$

where E_i is the initial potential, γ the voltage sweep rate in $V s^{-1}$ and t the time in seconds.

2.2 CHRONOPOTENTIOMETRY

The term chronopotentiometry is applied to the technique of electrolysis at constant current under the conditions of linear diffusion and the electrode potential is measured as a function of time.

The following conditions are to be satisfied.

1. The electrode is stationary and the area of the electrode remains unaltered during the course of the electrolysis.
2. The only mode of mass transport of reactants and products from and to the electrode is by diffusion.
3. Convection and migration are negligible.
4. The concentration of the depolariser at the beginning of the electrolysis, is uniform throughout the solution.
5. The speed of electrolysis is great as compared to the rate of diffusion.

6. The current is consumed only for the reduction and oxidation of solute electrolyte present in the solution.

In the technique of chronopotentiometry, since the current is constant, the electrolysis proceeds at a uniform rate. Now consider a fast electrode reaction $O + n\,e \rightleftharpoons R$, taking place under the above mentioned conditions. As soon as the electrolysis is initiated, the concentration of the electroactive species starts varying and the electrode shows the equilibrium potential of the solution in contact with it which varies with time.

The equilibrium potential of the electrode is given by the well known Nernst equation as

$$E = E^{o} + \frac{RT}{nF} \ln \frac{[Ox]_{el}}{[Red]_{el}} \qquad 2.2$$

where $[Ox]_{el}$ and $[Red]_{el}$ are the concentrations of oxidised and reduced species respectively at the electrode surface. During the electrolysis, the concentration of $[Ox]_{el}$ reduces steadily from C_o to zero, whereas the concentration of $[Red]_{el}$ increases steadily and reaches C_R.

As the electrolysis proceeds, the ratio of $[Ox]_{el}/[Red]_{el}$ decreases steadily because of the continuous decrease in $[Ox]_{el}$ species. This is because the diffusion is the only mode of mass transfer and the speed of electrolysis,

that is the rate of electron transfer is greater than the supply of $[Ox]_{el}$ at the electrode surface. The change will be slow as long as above mentioned ratio is not too different from unity but later a sudden jump in potential is shown indicating zero concentration of $[Ox]_{el}$ species at electrode surface. At this stage, the rate of diffusion of the oxidising species arriving at the electrode surface is insufficient to consume the entire current flowing between the electrodes and a second species if present in the solvent starts getting reduced, and ultimately the supporting electrolyte itself starts getting reduced when no more species are left available for reduction.

The time elapsed from the beginning of the electrolysis until this rapid potential change indicated by a sudden jump due to reduction of other ions is called ' transition time τ ' and this term was first introduced by Butler and Armstrong[52].

Sand first reported the existence of ' transition time ' and showed that in an unstirred solution and under the conditions of linear diffusion the transition time τ is related to concentration by the equation

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} n F A D^{\frac{1}{2}} C^{\infty}}{2i} \qquad 2.3$$

where τ = transition time in seconds

n = number of electrons exchanged during the electrode process (faradays mol^{-1})

F = faraday (96, 495 faraday C^{-1})

A = the area of the electrode in cm^2

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

i = the current in amperes

C^{∞} = concentration of the electroactive species in moles cm^{-3}

The Sand's equation is the fundamental equation of chronopotentiometry and is valid regardless whether or not the electrode process is reversible. The constancy of the product $i\tau^{\frac{1}{2}}/C$ has been verified by Gierst[53]. More work on this technique was reported by Delahay[54,55] and Reilley et. al[56].

Transition time in chronopotentiometry is equivalent to the limiting diffusion current in polarography. The square root of transition time is proportional to the bulk concentration of electroactive species and $E_{\tau/4}$ or quarter wave potential, in the case of mercury electrode is equivalent to $E_{\frac{1}{2}}$ or the polarographic half wave potential. Unfortunately the measurement of τ, which is the most important parameter in chronopotentiometry, like the limiting current in polarography, is not straight forward especially when the chronopotentiograms are poorly defined. The effect of double layer charging is difficult to eliminate in any simple way[57] but can safely be ignored if Sand's equation is obeyed. Usefulness of this technique in analytical chemistry arises from

the fact that square root of transition time is proportional to the bulk concentration of the solute in solvent.

2.2.1 Reversible Systems

An electrode process can be said to be reversible if the magnitudes of the forward and reverse reaction rate constants are large enough so that Nernst equation is obeyed. Sand's equation is applicable to any electrochemical reaction where the only mode of mass transport is by linear diffusion. Karaoglanoff[58] has given a relation applicable only to reversible processes where the oxidised and reduced species are soluble in the medium.

$$E = E_{\tau/4} - \frac{RT}{nF} \ln \frac{t^{\frac{1}{2}}}{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}} \qquad 2.4$$

where E is the electrode potential, t is the time in seconds after start of electrolysis, $E_{\tau/4}$ is the quarter wave potential i.e. the potential when $t = \tau/4$. When mercury is used as working electrode $E_{\tau/4}$ is related to the standard potential of the solute species by

$$E_{\tau/4} = E^{o} - \frac{RT}{nF} \ln \frac{f_r D_o^{\frac{1}{2}}}{f_o D_r^{\frac{1}{2}}} \qquad 2.5$$

where subscripts o and r stand for oxidised and reduced species respectively, f for activity coefficient.

Two things are clear from the equation 2.4

1. $E_{\tau/4}$ is independent of current and concentration.

2. A log plot of $(\tau^{1/2} - t^{1/2})/t^{1/2}$ vs E should yield a straight line whose reciprocal slope is $2.303\ RT/nF$ or $0.059/n$ at 298 K for a reversible process.

This method may be used to verify the reversibility of an electrode process and has been verified by Delahay[59].

2.2.2 Irreversible Systems

An irreversible process can be represented as $O + n\,e \longrightarrow R$. The current potential relationship for an irreversible electrode reaction is given by[60]

$$i = n\,F\,A\,C_o\,K^{\circ}_{f,h} \exp\left(\frac{-\alpha_c n_{\alpha c} FE}{R\,T}\right) \qquad 2.6$$

where α_c is the transfer coefficient of the electrode reaction, C_o is the concentrations of electroactive species at the electrode surface, $n_{\alpha c}$ is the number of electrons involved in the rate determing step. $K^{\circ}_{f,h}$ is the rate constant for the irreversible process in the forward direction expressed in $cm\,s^{-1}$ at E = 0 vs NHE. The other terms have their usual significance. This equation is valid only if the kinetics of the electron transfer reaction is controlled by a single rate determining step and rate of reverse process $K^{\circ}_{b,h}$ is negligible.

If the value of τ from Sand's equation is substituted the relation obtained[61] is

$$E = \frac{RT}{\alpha n_a F} \ln \left(\tau^{\frac{1}{2}} - t^{\frac{1}{2}} \right) + \frac{RT}{\alpha n_a F} \ln \frac{2K^{\circ}_{f,h}}{(\pi D)^{\frac{1}{2}}} \qquad 2.7$$

It can be concluded from the equation that log plot of $\tau^{\frac{1}{2}} - t^{\frac{1}{2}}$ vs E should yield a straight line with slope of $RT/\alpha n_a F$ and $E\,\tau/4$ for irreversible case varies linearly with ln C_o and current density (Amp cm^{-2}). The intermediate step is given by Reinmuth[60]. The values of αn_a and $K^{\circ}_{f,h}$ can be determined by the use of equation 2.7 or with the help of its another variation.

$$E = \frac{RT}{\alpha n_a F} \ln \frac{n A F C^{o} K^{\circ}_{f,h}}{i} + \frac{RT}{\alpha n_a F} \ln \left[1 - \left(t/\tau \right)^{\frac{1}{2}} \right] \qquad 2.8$$

2.2.3 Consecutive and Step-wise Processes

When a solvent is having more than one electroactive species, for each reduction, a corresponding inflection is obtained. Once the first electroactive species gets reduced, the reduction of second species begins but the first species still continues to diffuse to electrode surface and continues to react; therefore it requires a longer period to reach the second transition time τ_2.

The relation of the concentration of the second electroactive species to its corresponding transition time τ_2 is given as[62]

$$(\tau_1 + \tau_2)^{\frac{1}{2}} - \tau_1^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} n_2 F A D_2^{\frac{1}{2}} C_2^{o}}{2 i} \qquad 2.9$$

where the symbols have their usual meaning. τ_2 is measured from τ_1, i.e. $\tau_2 + \tau_1$ is the total time required for second inflection point.

An electroactive species may get reduced or oxidised in two stages. Each stage of reduction or oxidation corresponds to one inflection in chronopotentiogram. Suppose a two step reduction or oxidation of a species is under consideration then the following equation[63] may be applied.

$$\frac{\tau_2}{\tau_1} = \left(\frac{2 n_2}{n_1}\right) + \left(\frac{n_2}{n_1}\right)^2 \qquad 2.10$$

2.2.4 Electrode Kinetics

Delahay et. al[64,65] have worked in the field of chronopotentiometry concerned with the chemical reaction followed by electron transfer.

Most of the chemical reactions are associated with the electron transfer. A heterogeneous reaction occurs at the boundary between a conducting metal and the dielectric containing mobile charges though a chemical reaction goes to completion through a number of stages, the rate of the entire process is determined by the slowest partial reaction. The activation energy of an electrochemical reaction is

dependent of the electrode potential and can change whereas in a heterogeneous chemical reaction, the activation energy is fixed for fixed set of parameters, like concentration, temperature, etc.

An electrochemical reaction

$$Ox + n\,e \rightleftharpoons Red$$

can be explained as follows. The conditions are that it is assumed that both the species are soluble either in solvent or in electrode. Convection and migration are eliminated keeping the solution unstirred and adding large excess of supporting electrolyte. The electroactive species reach the electrode by semi-infinite linear diffusion at a certain rate which is determined by steady state condition and the electrons are exchanged at the electrode. The rate is determined by potential of the electrode.

In first order reaction, the rate of electron transfer is proportional to the concentration of the reactants at the electrode. If U_f and U_b are the forward and backward reaction velocities respectively and $K_{f,h}$, $K_{b,h}$ are the respective rate constants, then

$$U_f = K_{f,h}\left[Ox\right]_{el} \quad \text{and} \quad U_b = K_{b,h}\left[Red\right]_{el}$$

The relation[66] between rate of exchange of electrons on the electrode potential and velocity constant can be given as

$$K_{s,h} = K^{o}_{f,h} \exp\left[\left(\frac{-\alpha n_a F}{RT}\right)E^{o}\right] \qquad 2.11$$

$$(K_{s,h})_b = K^{o}_{b,h} \exp\left[\left(\frac{-\beta n_a F}{RT}\right)E^{o}\right] \qquad 2.12$$

where α is the transfer coefficient, $\beta = 1-\alpha$ and $K^{o}_{f,h}$, $K^{o}_{b,h}$ are rate constants for forward and reverse electrode reactions respectively at the potential E = 0 taken in NHE scale.

The transition time can be changed by varying the current density. The transition time should be selected in such a way that convection should not interfere with the deffusion and almost all the current should be utilised in electrode transfer process and negligible portion of the current should be utilised for double layer charging.

2.2.5 The Measurement of Transition Time and Quaterwave Potentials

The transition time 'τ' is defined as the time from the start of the electrolysis until rapid potential change takes place. The accuracy of chronopotentiometric method depends upon the exactness with which transition times can be measured. Assuming that the recorder is accurate, the problem is how to measure transition times from recorded curves. Because of the curvature caused by the charging of double layer it becomes, at times, difficult. Russel and Peterson[67] have given the details of different methods for the measurement of transition time.

The method given by Delahay and Berzins[61] is applicable to well defined curves and adopted here during the measurement of transition times. The method is illustrated in Fig. 2.1. Draw the tangent lines AE and ED and locate the point G where the potential time curve departs from a straight line. The transition time is then taken as GH. To find out the quarter-wave potential draw the horizontal lines AF and ED in Fig. 2.1. The points I and J are marked on these lines such that $EI = \frac{1}{4} ED$ and $AJ = \frac{1}{4} AP$. The line IJ is drawn across the potential time curve. The potential at point K is the quarter wave potential. This method of finding out the quarter-wave potential is that of Delahay and Mamantov[55]. They took LM as the transition time. The two methods may give slightly different results.

For measuring transition time when the curve is distorted, a practical method[5] is to construct the two tangent lines to locate point A (Fig. 2.2). AB is taken as transition time. But generally the method of locating point G is preferred[68], transition time being taken from G to extension of starting portion of the curve (Fig. 2.2).

2.2.6 Current Reversal Chronopotentiometry

One of the advantages of chronopotentiometry over polarography is that the reaction can be studied in both directions by reversing the direction of the current. If the reduction of substance O to R is carried out chronopotentiometrically

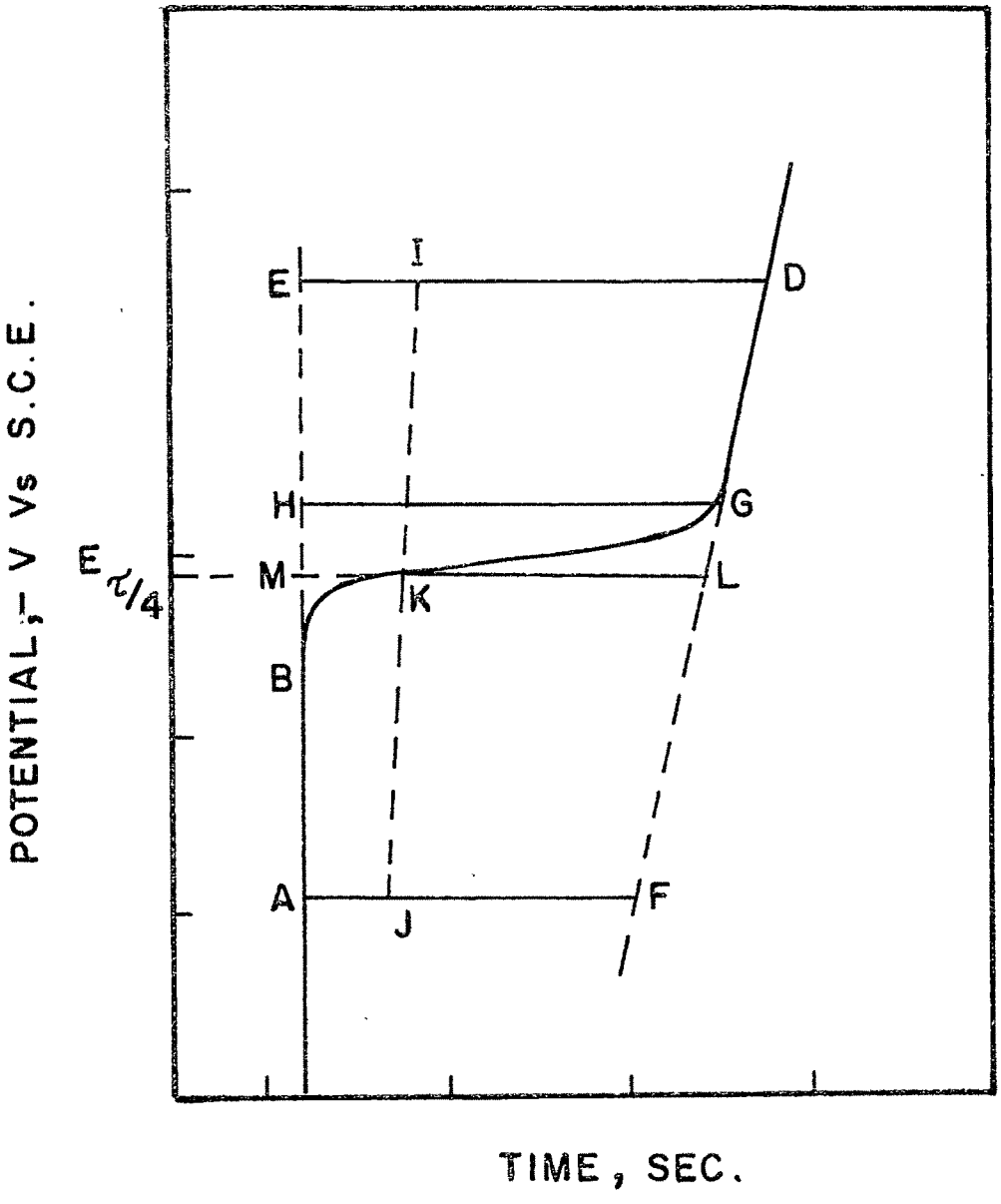

FIG. 2.1. METHOD OF TRANSITION TIME MEASUREMENT "REVERSIBLE" CURVE.

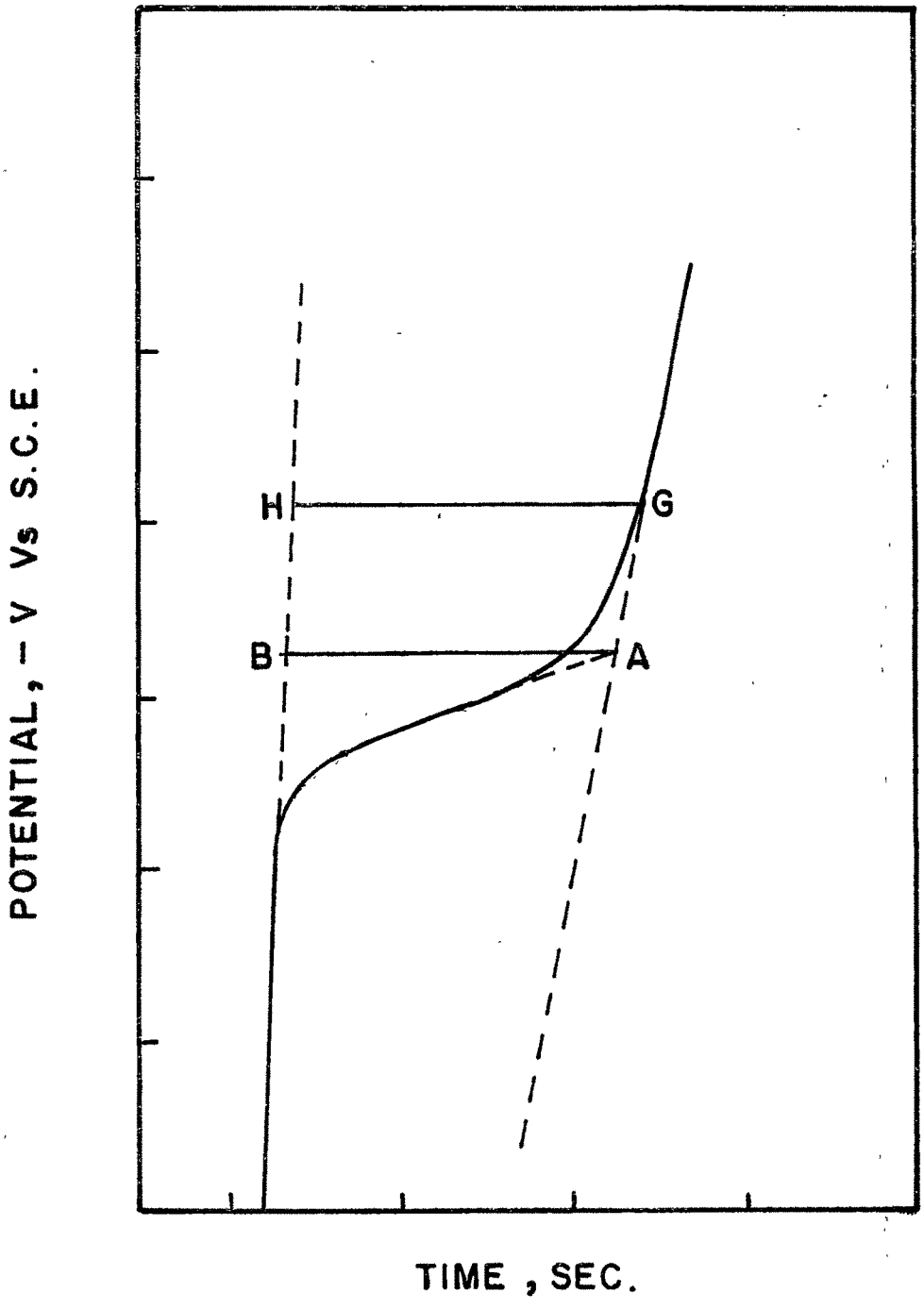

FIG. 2.2. METHOD OF TRANSITION TIME MEASUREMENT: DISTORTED CURVE.

in usual manner, but the constant current is reversed at or before the transition time for substance O, R may be reoxidised so that a reverse transition time is recorded and the potential time curve thus obtained can be treated quantitatively.(63) If the substance R is soluble in either the solution or the electrode and the magnitude of the constant current is equal in both directions, for a reversible process, the reverse transition time τ_r will be equal to one third of the forward electrolysis time τ_f. If the current is reversed exactly at the transition time, then $\tau_r = {}^1/_3 \tau_f$. This decrease in reverse transition time is due to the diffusion of a portion of R away from the electrode during electrolysis. If the diffusion is prevented by precipitating or plating R on the electrode surface, then τ_r will be equivalent to τ_f.

The equation for the reverse potential time curve for the case in which both O and R are soluble has been derived by Berzins and Delahay[63].

For a reversible reduction it is given as

$$E = E' + \frac{RT}{nF} \ln \frac{\tau^{1/2} - (\tau + t')^{1/2} - 2t'^{1/2}}{(\tau + t')^{1/2} - 2t'^{1/2}} \qquad 2.13$$

where t' is equal to $t - \tau$, other symbols having their usual significance. The potential analogous to $E_{\tau/4}$ is $E_{0.215/\tau}$[69]

In the case of an irreversible electrode reaction, equation 2.13 becomes

$$E = \frac{RT}{(1-\alpha)n_a F} \ln \frac{\pi^{\frac{1}{2}} D_r^{\frac{1}{2}}}{2 k^o_{b,h}} - \frac{RT}{(1-\alpha) n_a F} \ln \left[(\tau - t')^{\frac{1}{2}} - 2 t^{\frac{1}{2}} \right]$$

.... 2.14

where $k^o_{b,h}$ is the rate constant for reverse reaction. Since $k^o_{f,h}$ and α_{nq} can be found out from a forward chronopotentiogram and $k^o_{b,h}$ and $(1-\alpha)$ from a current reversal chronopotentiogram, a complete study of kinetics of electrochemical reaction can be made.

2.2.7 Diagnostic Criteria for Various Kinetic Schemes

In this section the diagnostic criteria and potential-time relations for various schemes in chronopotentiometry are quoted.

DIAGNOSTIC CRITERIA FOR VARIOUS KINETIC SCHEMES*

No.	Kinetic Scheme	Linear ln Plot	ln Plot Slope	$\partial E_{1/4} / \partial \ln i_o$	$\partial E_{1/4} / \partial \ln C^*$	τ_r / τ_f
1	$O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} R$	$(\tau^{1/2} - t^{1/2}) / t^{1/2}$	RT/nF	0	0	$1/3$
2	$O \underset{}{\overset{\text{slow}}{\rightleftharpoons}} R$	None	...	0 to $-RT/\alpha nF$	0 to $+RT/\alpha nF$	$1/3$
3	$O \longrightarrow R$	$\tau^{1/2} - t^{1/2}$	$RT/\alpha nF$	$-RT/\alpha nF$	$+RT/\alpha nF$	$1/3$ or 0
4	$O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} R$ (insol.)	$\tau^{1/2} - t^{1/2}$	RT/nF	0	+RT/nF	1
5	$O \underset{}{\overset{\text{slow}}{\rightleftharpoons}} R$ (insol.)	None	...	-RT/nF to $-RT/\alpha nF$	RT/nF to $RT/\alpha nF$	1
6	$O \longrightarrow R$ (insol.)	$\tau^{1/2} - t^{1/2}$	$RT/\alpha nF$	$-RT/\alpha nF$	$+RT/\alpha nF$	1 or 0
7	$O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} R \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} \gamma$	Same as No. 1	Same as No. 1	Same as No. 1	Same as No. 1	Same as No. 1
8	$O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} R \underset{}{\overset{\text{slow}}{\rightleftharpoons}} \gamma$	None	...	0 to -RT/nF	0 to +RT/nF	0 to $1/3$
9	$O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} R \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} \gamma$	$\tau^{1/2} - t^{1/2}$	RT/nF	-RT/nF	+RT/nF	0
10	$O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} R \underset{}{\overset{\text{slow}}{\longrightarrow}} \gamma$	None	...	0 to -RT/nF	0 to +RT/nF	0 to $1/3$
11	$mO \rightleftharpoons pR$	$(\tau^{1/2} - t^{1/2})^m / t^{p/2}$	RT/nF	0	(m - p)RT/nF	$1/3$
12	$2O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} 2R \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} \gamma$	Same as No. 11	Same as No. 11	Same as No. 11	Same as No. 11	...
13	$2O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} 2R \underset{}{\overset{\text{slow}}{\rightleftharpoons}} \gamma$	None	...	0 to -RT/3nF	-RT/nF to +RT/nF	0 to $1/3$
14	$2O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} 2R \underset{}{\overset{\text{rapid}}{\longrightarrow}} \gamma$	$(\tau^{1/2} - t^{1/2})$	RT/nF	-RT/3nF	+RT/nF	0
15	$2O \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} 2R \underset{}{\overset{\text{slow}}{\longrightarrow}} \gamma$	None	...	0 to -RT/3nF	-RT/nF to +RT/nF	0 to $1/3$

* Ref. (60), Table I

Potential - Time Relations for Various Kinetic Schemes*

No.

1 $E = E^{o'} + \frac{RT}{nF} \ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) / t^{\frac{1}{2}} + \frac{RT}{nF} \ln \phi$

3 $E = E^{o'} + \frac{RT}{\alpha nF} \ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) + \frac{RT}{\alpha nF} \ln 2K_s/(\pi D_o)^{\frac{1}{2}}$

4 $E + E^{o'} + \frac{RT}{nF} \ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) + \frac{RT}{nF} \ln 2i_o/nF (\pi D_o)^{\frac{1}{2}}$

6 E = same as No. 3

7 E = entry (No. 1) $+ \frac{RT}{nF} \ln (1 + K)$ $(D = D_R)$

8 E = entry (No. 1) $- \frac{RT}{nF} \ln \left[\frac{1}{1+K} + \frac{\pi^{\frac{1}{2}} K \operatorname{erf} (k_f + k_r)^{\frac{1}{2}} t^{\frac{1}{2}}}{(k_f + K_r)^{\frac{1}{2}} t^{\frac{1}{2}}} \right] (D = D_R)$

9 $E = E^{o'} + \frac{RT}{nF} \ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) + \frac{RT}{2nF} \ln (k_f/\pi)$

10 E = entry (No. 9) $- \frac{RT}{nF} \ln \operatorname{erf} (k_f t)^{\frac{1}{2}}$

11 $E = E^{o'} + \frac{RT}{nF} \ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})^m / tp/2 + \frac{RT}{nF} \ln (D_R / p^2)^p (m^2/D_o)^m + \frac{(m - p) RT}{nF} \ln (2i_o / nF \pi^{\frac{1}{2}})$

14 $E = E^{o'} + \frac{RT}{nF} \ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) + \frac{RT}{3nF} \ln (16 i_o k_f D_R / 3 \pi^{3/2} nF D_o^{3/2})$

* Ref. (60), Table II

2.3 CYCLIC VOLTAMMETRY

In cyclic voltammetry, a triangular voltage sweep is applied to the working electrode. This linearly variable voltage applied to the working electrode is then reversed at a predetermined potential, so that the product of electrode process formed during the forward sweep is electrolysed.

In a typical qualitative study, it is usual to record voltammograms over a wide range of voltage sweep rates and for various values of potentials. Commonly, there will be several peaks and by observing how they appear and disappear as the potential limits and sweep rates are varied. Also by noting the differences between the first and subsequent cycles, it is possible to decide how the processes represented by peaks are related. At the same time, from the sweep rate dependence of the peak amplitudes the role of adsorption, diffusion and coupled homogeneous reactions may be identified. The difference between first and subsequent cycles usually provide information about the mechanism of the electrode reaction. But for accurate kinetic data, it is the first sweep cyclic voltammogram which should be analysed.

Recently the technique has been gaining increasing importance[70,71] because of its utility in preliminary investigations of electrochemical processes and to eluciate electrode kinetics.

The three electrode system employed in cyclic voltammetry generally consists of hanging mercury drop, platinum disc, platinum, gold or silver wire, carbon, glassy carbon, tungsten, molybdenum as working electrodes. The reference electrode usually is calomel or silver - silver chloride and in most cases platinum is the auxiliary electrode.

Cyclic voltammetry is a diffusion controlled process, that is, the only mode of mass transport of the reactants and products to and from the electrode is by diffusion. The thermostated solution is kept unstirred to avoid convective mass transfer. The mass transfer due to migration is taken care of by addition of large amount of indifferent or supporting electrolyte which carries the bulk of the current.

On application of potential sweep to the working electrode with reference to the reference electrode, the current starts flowing between working electrode and auxiliary electrode and this current is measured as a function of time.

The reversible charge transfer process occuring here can be represented as

$$O + ne \rightleftharpoons R$$

The rate of electron transfer is much faster compared to the supply of electroactive species which is diffusion controlled.

2.3.1 Reversible Systems

For a reversible electrode reaction, the ratio of concentration of oxidised to reduced form of electroactive species is governed by the well known Nernst equation.

$$E = E^{o} + \frac{RT}{nF} \ln \frac{[Ox]_{el}}{[Red]_{el}} \qquad 2.2$$

and as the potential of working electrode is made increasingly negative, in order to satisfy the Nernst equation, the concentration of oxidised species must progressively decrease. This condition calls for the concentration gradient between the electrode surface and the bulk of the solution. According to Fick's law of diffusion, the concentration gradient results in enhancing the rate of diffusion of the electroactive species to the electrode and consequently the current flowing through the cell increases. As the rate of charge transfer at the electrode surface is fast in the case of a reversible process, the concentration of electroactive at the surface of the electrode soon becomes zero. At this point the concentration gradient is maximum and the current reaches to its maximum value.

The voltage sweep rate decides the shape of the I - E curve. The faster sweep rates give peaks and slow sweep rates result in plateau.

In cyclic voltammetry, after a forward voltage sweep a reverse voltage sweep is applied. During the reverse sweep the formation of R still continues until the potential has reached E^o value, at E^o R starts getting reoxidised back to O intiating a reverse flow of current so an anodic peak is developed in the same manner as the cathodic peak.

Randles[72] and Sevcik[73] have given a rigorous theoretical treatment and developed the mathematical relationship for a single scan method for a reversible reaction at a plane electrode. The equation known as Randles - Sevcik equation[74] is given as follows.

$$i_p = k n^{3/2} A D_o^{\frac{1}{2}} C_o \gamma^{\frac{1}{2}} \qquad 2.15$$

where i_p = peak current in amperes

D_o = diffusion coefficient in $cm^2 s^{-1}$

A = electrode area in cm^2

γ = voltage sweep rate $V s^{-1}$

C_o = concentration in moles cm^{-3}

k = Randles - Sevcik constant

The value of Randles - Sevcik constant[75] is generally taken as 2.69×10^5

k can also be calculated from $i - t^{\frac{1}{2}}$ curves from the following equation[74]

$$i_p = k n^{3/2} A D_o^{\frac{1}{2}} C_o \gamma^{\frac{1}{2}} \qquad 2.15$$

$$\text{also} \quad i t^{\frac{1}{2}} = \frac{n F A C_o D^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \qquad 2.16$$

$$\text{so} \quad i_p = i t^{\frac{1}{2}} \frac{(n \pi \nu)^{\frac{1}{2}}}{F} \times k \qquad 2.17$$

Thus by substituting known values, k can be easily calculated.

Nicholson and Shain[76] have given the following relationship for the instantaneous current on the peak polarogram as

$$i = n F A C_o (\pi D_o \sigma)^{\frac{1}{2}} \chi (\sigma t) \qquad 2.18$$

$$\text{where} \quad \sigma t = \frac{n F}{RT} \nu t = \frac{n F}{RT} (E_i - E) \qquad 2.19$$

The values of $\chi \sigma t$ were calculated by them as a function of σt or $n (E - E_{\frac{1}{2}})$ which may be substituted in equation 2.18 to get the instantaneous value of current. This may help to construct a theoretical current potential curve for linear sweep voltammetry.

For a reversible reaction at 298 K

$$n (E_p - E_{\frac{1}{2}}) = -28.5 \text{ mV} \qquad 2.20$$

and for this value of function $\pi^{\frac{1}{2}} \chi \sigma t$ and hence the current reaches its maximum value. After substituting this value of $\pi^{\frac{1}{2}} \chi \sigma t$ as 0.4463 given in Table 1 of Ref. 76 we get the relationship for peak current as

$$i_p = 0.4463 \, n F A C_o^{\,b} \left(\frac{nF}{RT}\right)^{\frac{1}{2}} \nu^{\frac{1}{2}} D_o^{\frac{1}{2}} \qquad 2.21$$

which at 298 K yields

$$i_p = 2.69 \times 10^5 \, n^{3/2} \, A D_o^{\frac{1}{2}} \, \gamma^{\frac{1}{2}} \, C_o \qquad 2.22$$

This equation indicates that for reversible reaction under semi-infinite diffusion conditions, the peak current i_p is proportional to square-root of sweep rate or

$$i_p / \gamma^{\frac{1}{2}} = \text{constant} \qquad 2.23$$

For a reversible process, peak potential and polarographic $E_{\frac{1}{2}}$ differ by $28.5/n$ mV at 298 K. The cathodic peak potential is $28.5/n$ more negative where as anodic peak potential is $28.5/n$ more positive than $E_{\frac{1}{2}}$.

It is also established that

$$E^p_{/2} - E_{\frac{1}{2}} = 28/n \text{ mV at } 298\,K \qquad 2.24$$

Now

$$n\,(E^p - E_{\frac{1}{2}}) = -28.5 \text{ mV} \qquad 2.25$$

and $E^p_{/2} - E_{\frac{1}{2}} = 28/n$ mV ;

so by combining these two equations

$$\left| E^p - E^p_{/2} \right| = \frac{56.5}{n} \text{ mV} \qquad 2.26$$

This equation is valid for cathodic and anodic waves. So far a cyclic voltammogram of a reversible system at 298 K the peak separation, $\triangle E^p$ will be

$$\triangle E^p = E^p a - E^p c = \frac{0.057}{n} \text{ V} \qquad 2.27$$

When the system is not behaving reversibly, the peak separation for cyclic voltammetry is more than $\frac{0.057}{n}$ V.

Nicholson[77] has used these ΔE^p values to calculate the heterogeneous rate constants k_s, for the charge transfer process. He correlated the ΔE^p values to the dimensionless parameter ψ which is defined by

$$\psi = \frac{\gamma^{\alpha} k_s}{[D_o \pi \gamma (nF/RT)]^{\frac{1}{2}}} \qquad 2.28$$

where $\gamma = D_o/D_R$, D_o and D_R are the diffusion coefficients of O and R in $cm^2 s^{-1}$, and α - the transfer coefficient, k_s - heterogeneous rate constant in $cm\, s^{-1}$, γ the voltage sweep rate in $V\, s^{-1}$.

Nicholson has worked out numerical values of ψ at different values of ΔE^p and these are found in Ref. 77.

2.3.2 Irreversible Systems

In the case of the reversible system discussed above the electron transfer rates at all potentials are significantly greater than the rate of mass transport and therefore Nernstian equilibrium is always maintained at the electrode surface. When the rate of electron transfer is insufficient to maintain this surface equilibrium the shape of a cyclic voltammogram changes. At low potential sweeps, the rate of electron transfer is greater than that of mass transfer and a cyclic voltammogram is recorded. As the sweep rate is

increased, however, the rate of mass transport increases and becomes comparable to the rate of electron transfer. The most noticeable effect of this is to increase peak separation. Whilst not normally done a useful way of studying data is to normalise the current for the change in the rate of diffusion. In addition to increasing peak separation with increasing sweep rate, the peak height is slightly reduced from that of a reversible system. In the limit for a totally irreversible process the shape of the cyclic voltammogram can be obtained mathematically by the solution of the differential equations given by

$$\frac{\partial C_o}{\partial t} = D_o \frac{\partial^2 C_o}{\partial x^2} \qquad 2.29$$

and

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} \qquad 2.30$$

Solutions of the above differential equations then yields the following equation for the peak current density at 298 K

$$I_p = (2.99 \times 10^5)\, n\, (\alpha_c n_\alpha)^{\frac{1}{2}}\, C_o^{\infty}\, D_o^{\frac{1}{2}}\, \gamma^{\frac{1}{2}} \qquad 2.31$$

where n_α is the number of electrons transferred upto and including the rate determining step; γ in this case is the voltage scan rate in volts/second and other symbols have the same significance as described earlier. Thus, as for a reversible case, the peak current density is proportional to the

concentration and to the square root of the sweep rate, but additionally to the square root of the transfer coefficient $\alpha_c n_\alpha$. For a one electron process and α_c equal to 0.5 the peak current for the reversible process is only 78.5% of a reversible one under the same conditions. The reason the peak is smaller is related to the shape of the peak. As the peak for an irreversible process is more drawn out the surface concentration of O changes more slowly with potential and at the instant when the surface concentration effectively reaches zero, the concentration profile for O is less steep and the flux to the surface lower.

The most marked feature of a cyclic voltammogram of a totally irreversible system is the total absence of a reverse peak. Such a feature above does not necessarily imply an irreversible electron transfer process, but could be due to a fast following chemical reaction. For a reversible case the value of E_p^c is independent of the sweep rate; for an irreversible case E_p^c is found to vary with the sweep rate according to the equation[77]

$$E_p^c = K - \frac{2.303\,RT}{2\alpha_c n_\alpha F} \log \gamma \qquad 2.32$$

where

$$K = E_c^\Phi - \frac{RT}{\alpha_c n_\alpha F}\, 0.78 - \frac{2.303}{2} \log \left(\frac{\alpha_c n_\alpha FD}{k_{s,h}^2 RT} \right) \qquad \ldots\ldots \quad 2.33$$

Thus at 298 K E_p^c drifts by $\frac{30}{\alpha_c n_\alpha}$ mV for each decade change in γ, the shift being in the negative direction as αn_α is increased. $|E_p - E_{p/2}|$ is also different for an irreversible case and is given by

$$\left|E_p - E_{p/2}\right| = \frac{48}{\alpha_c n_\alpha} \text{ at } 298\,K \qquad 2.34$$

A list of diagnostic criteria is given in the end of this section and if all of them are satisfied, the above equation can be used to calculate a value for $k_{s,h}$, the heterogeneous electron transfer rate constant at the formal potential.

It is also possible that a reversible process at a low sweep rates may become irreversible after passing through an intermediate state known as quasi-reversible. This transition occurs when the relative rate of electron transfer with respect to that of mass transport is insufficient to maintain Nernstian equilibrium at the electrode surface. In the quasi-reversible region both forward and back reactions make a contribution to the observed current and the region is generally recognised to have the following boundaries[78].

$$0.3\,\gamma^{\frac{1}{2}} \gg k_{s,h} \gg 2\times10^{-5}\,\gamma^{\frac{1}{2}} \text{ cm.s}^{-1} \qquad 2.35$$

The change from reversibility to irreversibility via quasi-reversibility can be readily recognised from a plot of I_p as a function of $\gamma^{\frac{1}{2}}$, if γ is changed several decades. To

obtain $k_{s,h}$ values from cyclic voltammetric data, mostly, the values of $n\Delta E_p$ are used as a function of ψ defined by

$$\psi = \frac{(RT)^{\frac{1}{2}} k_{s,h}}{(n F D \pi\gamma)^{\frac{1}{2}}} \qquad 2.36$$

By comparing experimental ΔE_p values with the working curve for several γ values, $k_{s,h}$ is readily obtained in favourable cases. In favourable cases, using a sweep rate of 1000 V s^{-1}, $k_{s,h}$ values as high as 1 cm s^{-1} can be determined.

A more descriptive approach to the problems of reversibility, quasi-reversibility and irreversibility follows.

The basic mechanism which is assumed is

$$O + ne \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R$$

Here k_f and k_b are heterogeneous rate constants of the electron transfer and are assumed to be functions of potential as expressed through the electrochemical absolute rate equation. The time dependence of the electrode potential is the form of an isosceles triangle. The above system is assumed to be initially in equilibrium. Both O and R are to be soluble either in the electrode or in to solution phase. To account for concentration polarization diffusion to a plane electrode is assumed to be the only source of mass transport. Mathematical formulation of this problem follows

$$\frac{\partial C_o}{\partial t} = D_o \frac{\partial^2 C_o}{\partial x^2} \qquad 2.29$$

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} \qquad 2.30$$

$t = 0,\ x \geqslant 0$

$$C_o = C_o^* ;\ C_R = C_R^* \qquad 2.37$$

$t \geqslant 0$

$$\lim_{x \to \infty} C_o = C_o^* ; \quad \lim_{x \to \infty} C_R = C_R^* \qquad 2.38$$

$t \geqslant 0,\ x = 0$

$$D_o \frac{\partial C_o}{\partial x} + D_R \frac{\partial C_R}{\partial x} = 0 \qquad 2.39$$

$$D_o \frac{\partial C_o}{\partial x} = k_f C_o - k_b C_R \qquad 2.40$$

With the electrochemical absolute rate equation, equation 2.40 can be transferred to

$$D_o \frac{\partial C_o}{\partial x} = k_{s,h} \, e^{-\frac{\alpha n F}{RT} (E - E^o)} \left[C_{o_{x=0}} - e^{nF/RT\,(E-E^o)} C_{R_{x=0}} \right] \qquad \ldots\ 2.41$$

Here E is the electrode potential, E^o is the standard potential, $k_{s,h}$ is the standard rate constant at E, α is the transfer coefficient and the remaining terms have their usual significance.

The potential in the above equation for the first scan (reduction) of the trangular wave takes the form

$$E = E_i - \gamma t \qquad 2.1$$

and for the second wave (oxidation)

$$E = E_i + \gamma t - 2\gamma\lambda \qquad 2.42$$

Here E_i is the initial equilibrium potential, γ is $\frac{dE}{dt}$ and λ is the period of the triangular wave.

If equations 2.41, 2.1 and 2.42 are combined the result is

$$D_o \frac{\partial C_o}{\partial x} = k_s \left(C_o^* / C_R^*\right)^{-\alpha} \left[S_{\lambda(t)}\right]^{-n} x$$

$$C_{o_{x=0}} - \left(C_o^* / C_R^*\right) S_{\lambda(t)} C_{R_{x=0}} \qquad 2.43$$

The function $S_{\lambda(t)}$ is defined as

$$S_{(t)} = \begin{cases} e^{-at} & t < \lambda \\ e^{at - 2a\lambda} & t > \lambda \end{cases} \qquad 2.44$$

where $$a = \frac{nF\gamma}{RT} \qquad 2.45$$

Equation 2.43 is the final form of boundary condition of 2.40 .

A function ψ can be derived where it can be shown that

$$\psi = \frac{\gamma^{\alpha} k_s}{\sqrt{\pi_a D_o}} = \frac{\gamma^{\alpha} k_s}{\sqrt{\pi \frac{nF}{RT} D_o}} \qquad 2.46$$

For large values of ψ (large k_s or small ν) the reaction becomes independent of ψ and α and reduces to the corresponding equation for reversible (Nernstian) electron transfer[76]. If the value of ψ approaches 0, the condition which is obtained is for a totally irreversible electron transfer. The intermediate case, which is of interest here, is described completely by the equation

$$\frac{x(y)\left[r\,(C_o^*/C_R^*)\,S_a(y)\right]^{\alpha}}{\psi} = 1 - S_a\lambda(y) - \int_0^y \frac{x(t)\,dt}{y-z}$$

$$- \gamma\,(C_o^*/C_R^*)\,S_a\lambda(y)\int_0^y \frac{x(t)\,dt}{y-z} \qquad 2.47$$

where $\gamma = (D_o / D_R)^{\frac{1}{2}}$

The above equation can not be solved analytically. Although a solution in the form of an infinite series can be obtained, series solutions for more than one half cycle become hopelessly complicated. The only practical approach,

therefore, which for the present case can be applied without loss of generality, is numerical evaluation. The method used by DeVries and VanDalen[79] involves less computational time for comparable accuracy.

The Nernstian approach limit to the reaction occurs when ψ [77] which is in good agreement with the calculations of Matsuda and Ayabe[78], when $\psi < 7$ the current voltage curves are dependent on both the values of ψ and α. For sufficiently small ψ (k_s very small or ν very large) the back reaction for electron transfer is unimportant and the processes for oxidation and reduction can be treated separately as the totally irreversible case. For intermediate values of ψ, i.e., for the region sometimes referred to as quassi-reversible, the form of the current voltage curves depends markedly on the exact values of ψ and α. The value of α affects the symmetry of the curves. For $\alpha < 0.5$ the cathodic peak is more rounded then the anodic peak. The broadening also results in the lowering of the peak height. For $\alpha > 0.5$ the reverse holds. Another effect involves the slight displacement of the waves along the potential axis. As α decreases, the cathodic peak is displaced cathodically. As the cathodic peak shifts cathodically with decrease of α, the anodic peak also shifts cathodically. Therefore in terms of differences of peak potentials $\triangle E^p$ changes in α tend to cancel. Thus the values of $\triangle E^p$ are very nearly independent of α in the

range $0.3 < \alpha < 0.7$. The extent to which this holds good depends on the exact value of ψ . Naturally as ψ increases, the approximation becomes increasingly good. The exact variation of peak potentials with ψ can be calculated from a knowledge of ΔE^p and n. This gives quantitatively the relationship between peak potentials, scan rates and electron transfer rate. For the successful use of this method, a scan rate is selected which gives an experimental value of ΔE^p in the useful range. From the experimental value of $\Delta E^p \times n$, the corresponding value of ψ is obtained and then k_s can be calculated with a knowledge of scan rate using equation 2.46. Actually to apply equation 2.46 rigorously γ^{α} also must be known. However, except for the unusual case of very large differences between D_o and D_R, the quantity γ^{α} is very near unity, regardless of α. The upper limit of rate constants measurable with cyclic voltammetry therefore depends on several factors. The most important of these is probably conductivity of the solution under investigation. With electrolytes of reasonably high conductivity, it should be possible to measure rate constants as large as 1 to 10^{-5} cm. s^{-1}.

2.3.3 Coupled Homogeneous Reactions

Cyclic voltammetry is probably the most powerful technique for investigating coupled chemical reactions. This technique helps one to get not only kinetic data, but also the

detection and identification of reaction intermediates. In such cases it is often necessary to have sweep rates ranging from 10 mV s^{-1} to a few hundred V s^{-1}. This enables first order rate constants in the range $1 - 10^4$ cm s^{-1} to be determined while for second order processes by choosing the conditions carefully it is possible to study reactions with rates close to the diffusion controlled limit.

The various types of reaction which can be studied by this technique include the coupled electrochemical reactions, electrochemical coupled reactions, catalytic reactions, the electrochemical coupled electrochemical reactions etc. The diagnostic criteria for these types and methods of computing electron transfer rate constants are described fully in Chapter 4 and 5. By and large such types of reactions are met with in organic chemistry and hence a detailed discussion is out of context in this study.

2.3.4 Surface Processes

Cyclic voltammetry has proved a very useful technique for the quantitative investigation of reactions involving adsorption processes which include not only adsorption, but deposition, passivation, corrosion, homogeneous redox catalysis etc.

Besides normal cyclic voltammetry at microelectrodes, the techniques of derivative cyclic voltammetry[80-82], a.c.

cyclic voltammetry[83-85], convolution cyclic voltammetry[85-90] etc. are also in vogue and can be used for specialised studies of complex reactions.

In section 2.3.5 are given the various diagnostic criteria for cyclic voltammetry for various kinetic schemes.

2.3.5 Diagnostic Criteria

Diagnostic criteria for cyclic voltammograms of reversible process at 298 K

1. $\triangle E_p = E_p^a - E_p^c = 59/n$ mV
2. $|E_p - E_{p/2}| = 59/n$ mV
3. $|I_p^a / I_p^c| = 1$
4. $I_p \propto \gamma^{1/2}$
5. E_p is independent of γ
6. at potentials beyond E_p, $I^{-2} \propto t$

Diagnostic tests for cyclic voltammograms of quasi-reversible systems at 298 K

1. $|I_p|$ increases with $\gamma^{1/2}$ but not proportional to it.
2. $|I_p^a / I_p^c| = 1$ provided $\alpha_c = \alpha_a = 0.5$
3. $\triangle E_p$ is greater than $59/n$ mV and increases with increasing γ.
4. E_p^c shifts negatively with increasing γ.

Diagnostic tests for cyclic voltammograms of totally irreversible system at 298 K

1. No reverse peak
2. $I_p^c \propto \gamma^{\frac{1}{2}}$
3. E_p^c shifts - 30 $\alpha_c n_\alpha$ mV for each decade of increase in γ.
4. $\left| E_p - E_{p/2} \right| = 48 \ \alpha_c n_\alpha$ mV.

2.4 CHRONOAMPEROMETRY

Chronoamperometry is one of the most important transient electrochemical techniques. In this technique, an instataneous perturbation of the electrode potential is applied and the system is monitored as it relaxes towards its new steady state to attain the equilibrium. In other words, the potential of the working electrode is changed instantaneously and the current - time response is recorded. In the process there is variation of rate of mass transport with the time elapsed. The kinetic parameters of the system are obtained by interpreting the data available over a wide range of variables therein and by using the curve fitting procedure.

In this technique and in it's allied techniques the mass transport of electroactive species is solely under diffusion controlled conditions, and the other modes of mass transport such as convection and migration under electrostatic attractive forces are eliminated.

2.4.1 Reversible Systems

Normally one encounters two different cases :
1. the electrode reaction is so rapid in comparison with the diffusion process that electrochemical equilibrium is achieved at the electrode and the Nernst equation can be applied (reversible process) and (2) the kinetics of the electrode reaction must be considered and the electrode process is said to be irreversible.

If the reaction $O + n\,e \rightleftharpoons R$ is considered, with R soluble either in solution or in the electrode, the current-potential characteristic of this reaction will be established on the assumption that each diffusing particle is a point, there being no interaction between particles in solution. Conditions for electrolysis are characterised as follows. The Nernst equation is supposed to be valid and consequently the ratio of the concentration of O and R at the electrode surface at a given potential is constant. Furthermore there is conservation of mass at the electrode surface during electrolysis and the sum of the fluxes of substances O and R at the electrode surface is zero. Once the concentrations are known the current is readily deduced from the flux of substances O at the electrode. Thus, the current i at potential E when no substance R is initially present in solution is

$$i = i_d \frac{1}{1 + (D_r/D_o)^{\frac{1}{2}} (f_o/f_r) \exp.\left[\left(\frac{nF}{RT}\right)(E - E_o)\right]} \qquad 2.48$$

with $i_d = \left[(n F A D_o^{\frac{1}{2}} / \pi^{\frac{1}{2}} t^{\frac{1}{2}}) \right] C$ 2.49

Here, the f's are the activity coefficients and t is the time elapsed since the beginning of the electrolysis in seconds. The other symbols have the same significance as earlier.

Since the ratio C_o / C_R of concentrations at the electrode surface approaches zero as E approaches $-\infty$, molecules or ions of substance O are reduced as soon as they reach the electrode. Under this condition i_d / A is called the diffusion current density.

The current-potential characteristics can now be constructed from values of i / i_d at different potentials but always for the same time. The corresponding equations obtained are similar to the ones obtained for polarography for reversible systems, viz.,

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \left[\frac{i_d}{i} - 1 \right] \qquad 2.50$$

with the half wave potential $E_{\frac{1}{2}}$ being given by

$$E_{\frac{1}{2}} = D^o + \frac{RT}{nF} \ln \frac{f_o}{f_R} \left[\frac{D_R}{D_o} \right]^{1/2} \qquad 2.51$$

The variable time t does not appear in the above equations because i_d / i is independent of t. However i and i_d depend on t. Nonplanar electrodes lend themselves to the same type of analysis. Spherical and cylindrical electrodes have been treated[54], with the limitation being that $t < 1$ sec. to

allow application of the above equations when $t/r^2 < 1$, where r is the radious of curvature.

2.4.2 Irreversible Systems

Numerous electrode systems are not reversible at the current densities prevailing in chronoamperometry. Electrochemical equilibrium is not achieved, i.e., the Nernst equation cannot be applied to correlate the electrode potential with the concentration of the reactants. The current - potential - time characteristic is obtained by consideration of the electrode process as a heterogeneous reaction with two steps in series; the electrode reaction proper and diffusion of the reactant and the product of electrolysis.

If the species involved in the reaction $O + n\,e \rightleftharpoons R$ are soluble, then the net rate is of the form $k_f C_o - k_b C_b$ where the C's are the concentrations at the electrode surface and the k's the rate constants for the forward and backward electrode reactions in units $cm\,s^{-1}$. If the back reaction can be neglected

$$i/i_d = \pi^{\frac{1}{2}}\,\lambda\,\exp(\lambda^2)\,erfc(\lambda) \qquad 2.52$$

$$\text{with } \lambda = \frac{k\,t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}} \qquad 2.53$$

The error function complement is defined by

$$erfc(\lambda) = 1 - (2/\pi^{\frac{1}{2}}) \int_0^{\lambda} e^{-x^2}\,dz \qquad 2.54$$

Thus the relationship between the current and the rate constant k_f is fully determined by equation 2.52. A plot of i/i_d against λ will show that i/i_d increases with λ, i.e., with k_f for a given time t. i/i_d is zero for $\lambda = 0$. When $i/i_d \longrightarrow 1$ for $\lambda \rightarrow \infty$ and the current tends to be solely diffusion controlled when the rate constant is sufficiently large. The approximate limits of $10^{-5} < k_f < 10^{-2}$ cm s^{-1} represent the range of rate constants that can be determined by polarography. Somewhat higher values of k_f (< 1 cm s^{-1}) can be determined by chronoamperometry for current - time curves recorded for shorter times ($t > 10^{-4}$s) than in polarography. The shape of the irreversible E - i curves depend on the relationship between the rate constant k_f and the electrode potential. Thus the rate constant k_f at any potential along the ascending segment of the i - E curve can be computed from the experimental value of i/i_d at a given time using equation 2.53 and 2.54. The value of D_o needed in the calculation of k_f from λ is computed from the diffusion current density by application of equation 2.53.

As a first approximation one has

$$k_f = k_f^o \exp \frac{-\beta R E}{RT} \qquad 2.55$$

where k_f^o is the value of k_f at E = 0 V (vs NHE) and β is a factor depending on the electrode reaction and electrolysis conditions. The rate constant k_f also can be expressed in

terms of the exchange current density and the overvoltage. The foregoing expression for k_f is only approximate because the structure of the double layer, however, will be essential in the inpretation of the salt effect on i - E characteristics for irreversible processes.

The i - E curves for irreversible systems can be represented approximately by equation 2.55 in which the factor β is substituted for n. The $E_{\frac{1}{2}}$ for irreversible i - E curves is not given by equation 2.51, since kinetic considerations were not introduced in the derivation of this equation. The potential $E_{\frac{1}{2}}$ of an irreversible curve depends on t. By definition $i / i_d = 0.5$ at $E_{\frac{1}{2}}$, since

$$\lambda = \frac{k_f t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}} \qquad 2.56$$

$k_f t^{\frac{1}{2}}$ must be constant at $E_{\frac{1}{2}}$ and consequently k_f is inversely proportional to $t^{\frac{1}{2}}$. The potential $E_{\frac{1}{2}}$ varies accordingly with $\ln t^{\frac{1}{2}}$, since k_f is an exponential function of E. The extension of the foregoing analysis by consideration of the forward and backward reactions follows the same pattern.

An excellent discussion on chronoamperometry has been given by Delahay[91].

2.5 SAMPLED CURRENT VOLTAMMETRY

A novel extension of chronoamperometry is sampled current voltammetry[92]. In this technique the experiment is

conducted in the same way as that in the case of chronoamperometry, but instead of application of a single potential step in the Cottrell region, a series of potentials steps are applied starting from the potential at which no faradaic process occurs, upto and beyond the Nernstian region till there is no change in the i - t plot for the next potential step applied. The initial potential is, however, maintained at a preset value, which is the same for all experiments. At this value no charge transfer at the electrode takes place.

The current is then sampled at a fixed time interval τ after the start of each step and the current $i_{(\tau)}$ is plotted against the respective potential. The current - potential curve thus obtained has a wave shape that is much similar to plot obtained by steady - state voltammetry.

This technique[85] has gained much importance recently because it enables to determine the half wave potentials of the electroactive species with ease. The technique is also a convenient means of evaluating the kinetic information about the redox system and the kinetic parameters such as k_f, k^o, $\alpha_c n_\alpha$, etc. can be deduced by this method.

2.5.1 Reversible systems

In the case of reversible process, the current at any given point $i_{(\tau)}$ on $i_{(\tau)}$ - E curve is given by

$$i_{(\tau)} = \frac{i_{d(\tau)}}{1 + (D_O/D_R)^{\frac{1}{2}} \exp\left[\frac{nF}{RT}(E - E^O)\right]} \qquad 2.57$$

The shape of the curve can be described by the above equation. The current $i_{d(\tau)}$ is the current at the time for the potential step at which the electrode process is proceeding under diffusion controlled conditions. As the value of potential step approaches the E^O value, the denominatior in the equation 2.57 progressively decreases. As the current $i_{(\tau)}$ increases steadily when $E = E^O$, the exponent part of the denominator in the above mentioned equation becomes equal to one, and at this point usually $D_O/D_R \simeq 1$, the current $i_{(\tau)} = \frac{i_{d(\tau)}}{2}$ and the value of potential step applied is the value of half wave potential.

The equation 2.57 may be rewritten as

$$E = E^O + \frac{RT}{nF} \ln \frac{D_R^{\frac{1}{2}}}{D_O^{\frac{1}{2}}} + \frac{RT}{nF} \ln \frac{i_{d(\tau)} - i_{(\tau)}}{i_{(\tau)}} \qquad 2.58$$

when $i_{(\tau)} = \frac{1}{2} i_{d(\tau)}$, we get half wave potential as

$$E_{\frac{1}{2}} = E^O + \frac{RT}{nF} \ln \frac{D_R^{\frac{1}{2}}}{D_O^{\frac{1}{2}}} \qquad 2.59$$

Thus

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \frac{i_{d(\tau)} - i_{(\tau)}}{i_{(\tau)}} \qquad 2.60$$

2.5.2 Irreversible Systems

In the case of an irreversible electrode process of the type $O + n e \longrightarrow R$, the anodic component is negligible and the equation for the current is given as

$$i = n F A C_o^* \; k_f \exp\left(\frac{k_s^2 t}{D_o}\right) \operatorname{erfc}\left[k_f \left(t/D_2\right)^{\frac{1}{2}}\right] \quad \ldots\ldots \quad 2.61$$

This could be rewritten as

$$i = \left(\frac{n F A D_o^{\frac{1}{2}} C_o^*}{t^{\frac{1}{2}}}\right) \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda) \qquad 2.62$$

where $\lambda = k_f t^{\frac{1}{2}} / D_o^{\frac{1}{2}}$

or $i = i_d \pi^{\frac{1}{2}} \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda)$ 2.63

For a given potential step experiment k_f and D_o are constant. So λ is proportional to time. Also, in the case of sampled current voltammetry, the time λ is fixed, hence λ becomes the function of the applied potential step, as k_f is also proportional to the applied potential step.

In the case, when current is governed both by mass transfer and charge transfer the current is given by the following equation

$$\frac{i}{n F A} = D_o \left(\frac{C_o(x, t)}{dx}\right)_{x=0} = k_f C_o(0, t) - k_b C_R(0, t) \quad \ldots\ldots\ldots \quad 2.64$$

where $k_f = k^o_e - \alpha naf(E - E^o)$

and $k_b = k^o_e (1-\alpha) naf (E - E^o)$

where $f = \frac{F}{RT}$

Now, by applying Laplace transform and taking inverse of it we get,

$$i_{(t)} = nFA k_f C_o^o \overset{e}{exp} (H^2 t) \text{ erfc } (H t^{\frac{1}{2}}) \qquad 2.65$$

where $H = \frac{k_f}{D_o^{\frac{1}{2}}} + \frac{k_b}{D_R^{\frac{1}{2}}}$

However, when anodic component of the reaction is negligible for the irreversible reaction, the equation 2.65 becomes

$$i = nFAC_o^o k_f \exp \left(\frac{k_f^2 t}{D_o} \right) \text{erfc} \left(\frac{k_f t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}} \right) \qquad 2.66$$

Now,

$$i = \frac{nFAD_o^{\frac{1}{2}} C_o}{t^{\frac{1}{2}}} \left(\frac{k_f t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}} \right) \exp \left(\frac{k_f^2 t}{D_o} \right) \text{erfc} \left(\frac{k_f t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}} \right),$$

..... 2.67

that is

$$i = i_d \pi^{\frac{1}{2}} \left(\frac{k_f t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}} \right) \exp \left(\frac{k^2_f t}{D} \right) \text{erfc} \left(\frac{k_f t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}} \right) \qquad 2.68$$

$$\frac{i}{i_d} = \pi^{\frac{1}{2}} \lambda \exp (\lambda^2) \text{ erfc } (\lambda) \qquad 2.69$$

where $\lambda = \frac{k_f t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}}$

In the case of argument λ larger than unity

$$\exp(\lambda^2)\,\mathrm{erfc}(\lambda) = \frac{1}{\pi^{\frac{1}{2}}\lambda}\left\{1 - \frac{}{2\lambda^2} + \frac{1\times 3}{(2\lambda^2)^2} - \frac{1\times 3\times 5}{(2\lambda^2)^3} \cdots\cdots\right\} \quad 2.70$$

By substituting the value of function in equation

$$\frac{i}{i_d} = \left\{1 - \frac{1}{2\lambda^2} + \frac{3}{(2\lambda^2)^2} - \frac{15}{(2\lambda^2)^3} + \cdots\cdots\right\} \quad 2.71$$

By approximation of right hand side to the first two terms, as the other terms would be insignificant

$$\frac{i}{i_d} = 1 - \frac{1}{2\lambda^2} \quad 2.72$$

On substituting the value for

$$\frac{i}{i_d} = \frac{2k_f{}^2 t - D_o}{2k_f t} \quad 2.73$$

For sampled-current voltammogram this may be given as

$$\frac{i_{(\tau)}}{i_{d_{(\tau)}}} = \frac{2k^2_f \tau - D_o}{2k^2_f \tau} \quad 2.74$$

and

$$k^2_f = \frac{D_o}{2\tau\left[1 - \frac{i_{(\tau)}}{i_{d_{(\tau)}}}\right]} \quad 2.75$$

or

$$k_f = \frac{D_o^{\frac{1}{2}}}{\sqrt{2}\,\tau^{\frac{1}{2}}\left[1 - \frac{i_{(\tau)}}{i_{d_{(\tau)}}}\right]^{\frac{1}{2}}} \quad 2.76$$

$$\text{So} \quad k_{f,h} = \frac{D_o^{\frac{1}{2}}}{2\tau^{\frac{1}{2}}} \times \left[\frac{i_{d(\tau)}}{i_{d_{(\tau)}} - i_{(\tau)}}\right]^{\frac{1}{2}} \qquad 2.77$$

In order to evaluate k_f for any electrochemical process the following procedure is to be followed.

At any τ the $i_{(\tau)}$ values are measured from the $i_{(\tau)} - E$ plot. The k_f values for the respective potentials are calculated. As we know

$$k_f = k^o \exp\left[\frac{-\alpha n_a F}{RT}(E - E^o)\right] \qquad 2.78$$

$$\log k_f = \log k^o - \frac{\alpha n_a F}{2.303\,RT}(E - E^o) \qquad 2.79$$

This means that if we plot log k_f vs E, the slope of the curve ($-\alpha n_a F/RT$) gives the value of αn_a and the intercept on the log k_f axis gives the value of k^o, the heterogeneous reaction rate constant.

The sampled current voltammetry can, thus, be utilized for calculating kinetic parameters of irreversible electrochemical reactions also. This subject is a natural corollory of chronoamperometry and as in chronopotentiometry and cyclic voltammetry reversal techniques can be employed, where an additional step or even a complex sequence of steps can be applied after the application of an initial potential step. The Nernstian behaviour of the potential step

reversal[93,94] for a reversible process and that of a quasi-reversible behaviour[95,96] have been recently treated and the extensive theoretical results compared with experimental data.