CHAPTER 4

Charge Transfer Kinetics and Diffusion

4.1   INTRODUCTION

In the last chapter, the measurement of thermodynamic properties (n, E^f, K) of interfacial charge transfer was discussed. These measurements completely describe the interfacial behaviour (for example the change of E with concentration of Ox or R) *if the electron transfer between the electrode and the redox species takes place at sufficiently fast rate.* This condition is indeed noticed in a number of cases. However, there are equally a good number of cases where the **charge transfer is slow.** It would be interesting to measure the rate parameters of such slow charge transfer processes. Since LSV and CV are known transient techniques it would also be worth measuring the charge transfer kinetics of even faster processes using such techniques. As seen in this chapter, these techniques are indeed very well-suited for such measurements.

If the electron transfer takes place in a single step, the entire kinetics is defined by just two parameters $k_h{}^o$ and β (Section 4.2.1). Multistep processes can be described using closely related parameters i_o and α. In addition, stoichiometric number v and reaction order for all reacting species are also defined (Section 4.2.2). Reversible chemical equilibria can influence the peak potential behaviour of such processes (Section 4.2.3). A number of associated chemical reactions can also be slow and their kinetics can influence LSV and CV behaviour. Studies of such slow chemical reactions are so important that they deserve a separate chapter (Chapter 5).

The thermodynamic properties of any overall redox reaction are independent of the electrode material used (these are reactions where all the reactive species are in solution). However, the electron transfer kinetics can depend very much on the electrode material. The methods discussed here (Section 4.3) may be directly employed to measure kinetic parameters on various electrode materials and hence establish surface effects. However, the physical chemistry involved in such catalysis and inhibition effects of electrode materials require more detailed cansideration and hence treated separately later (Chapters 11 to 14).

Two redox couples (say Ox_1/R_1 and Ox_2/R_2) may interact among them at the electrode surface. The electron released by one couple to the electrode may be taken up by another couple from the electrode. The kinetics of such mixed potential processes [1, 2] may

also be considered in this chapter. However this model was first proposed [3] and is still extensively employed in surface processes and hence solution-phase mixed potential processes shall be considered with their metal-mixed potential analogs (Chapter 12).

4.2 THE MODEL

4.2.1 SINGLE STEP CHARGE TRANSFER KINETICS

Again consider the general electron transfer reaction (equation 4.1) and now concentrate on the kinetic aspects:

$$Ox + ne \rightleftharpoons R \qquad 4.1$$

The rate equation for this electrochemical reaction is formally similar to the usual chemical reaction

$$v = k_f C_{Ox}(o, t) - k_b C_R(o, t) \qquad 4.2$$

In this expression, v is rate of the reaction; k_f and k_b are the rate constants of the forward and reverse reactions respectively; $C_{Ox}(o, t)$ and $C_R(o, t)$ are the surface concentrations of Ox and R ($x = o$) at time t respectively. Although formally similar, this rate expression has some subtle but important differences when compared with the chemical reaction:

i) The electron transfer is a heterogeneous surface process. Here v has the units of moles. $cm^{-2} sec^{-1}$. (For a homogeneous chemical reaction v has the unit of mole $cm^{-3} sec^{-1}$). Since concentrations are expressed in moles cm^{-3}, the rate constants k_f and k_b of an electrochemical reaction must have the dimension of cm. sec. For a first order chemical reaction k_f, k_b would have the unit of sec^{-1}.

ii) In the chemical reactions, evaluation of rate v itself is a tedius process. One must monitor the change in concentration of the reacting species with respect to time, draw a C versus t plot and find out the slope at each concentration to obtain the rate. In electrochemical reactions, the current at any potential is a direct measure of the electron transfer rate.

$$\frac{i}{nFA} = v \qquad 4.3$$

where i is the current, F is the faraday constant (96, 490 coulombs) and A is the area of the electrode surface.

iii) The most important difference, of course, is that the rate of a chemical reaction can easily be altered by varying the electrode potential. k_f and k_b of electron transfer reactions can also be varied by varying T and P as in the case of ordinary chemical reactions. However, they can be easily varied by changing the electrode potential E.

$$k_f = k^o{}_f \exp (-\beta n f E) \qquad\qquad 4.4$$

$$k_b = k^o{}_b \exp (1 - \beta) n f E \qquad\qquad 4.5$$

where $k^o{}_f$, $k^o{}_b$ are the rate constant when $E = 0$ and $f = F/RT$. Proper understanding of symmetry factor β in these expressions is quite essential and basic in electrode kinetics. This is the fraction of the electrical part of the free energy (nFE) applied to the system which activates the activation complex [4-6] (see Fig. 1.8) for the forward reaction. Although β can have any value between 0 and 1 depending on the potential energy profiles of the reactants and products (Fig. 1.8), they generally range around 0.5. It is generally assumed that β is potential independent. However, statistical mechanical theories [7, 8] do suggest variation of β with E. As we shall see later, potential dependence of β has also been experimentally established in a few fast electron transfer processes (Section 4.4.2).

Figure 1.8 also indicates that when the electrical potential E accelerates the reaction in one direction, it simultaneously retards the reaction in the opposite direction. Suppose we increase the potential in the negative direction, k_f would increase and k_b would decrease.

At the formal electrode potential (E^f) the forward and reverse rate constants must be equal since no net reaction should take place at this potential when the concentration terms are unity (equation 4.2). Hence

$$k^o{}_f \cdot \exp (- \beta \, n f E^f) = k^o{}_b \cdot \exp (1 - \beta) \, n f E^f$$

$$= k^o{}_h \qquad\qquad 4.6$$

$k^o{}_h$ defined by equation 4.6 is the standard heterogeneous rate constant. This is the charge transfer rate constant at the equilibrium poten-

tial. For fast processes, k_h^o may have values up to 10 cm/sec [9] and for slow processes, k_h^o can have values as low as 10^{-9} cm/sec (for example hydrogen evolution reaction on Hg) [10].

The potential dependence of rate constant can be expressed by substituting equation 4.6 in equation 4.2.

$$v = k_h^o [C_{Ox} (o, t) \exp - \{\beta \, nf \, (E - E^f)\}$$

$$- C_R (o, t) \exp \{(1 - \beta) \, nf \, (E - E^f)\}] \qquad 4.7$$

At equilibrium (E_{eq}) the net rate must be zero and the forward and reverse reaction rates must be equal to its value in the bulk. Thus, the concentration of Ox and R at the surface would be equal to its value in the bulk

$$nF \, k_h^o \, C_{Ox} \exp \{ - \beta \, nf \, (E_{eq} - E^f)\}$$

$$= nF \, k_h^o \, C_R \exp \{(1 - \beta) \, nf (E_{eq} - E^f)\}$$

$$= i_o \qquad 4.8$$

Equation 4.8 defines another important parameter, i_o, the exchange current density which is the rate of electron exchange between the electrode and the redox species at the equilibrium potential. Note that i_o represents a dynamic exchange rate. Although there is exchange of electrons in both the directions of the interface, the exchange rates on both the directions are equal and opposite and hence the net exchange is zero.

From equation 4.8 we may obtain

$$\frac{C_{Ox}}{C_R} = \exp \, nf(E_{eq} - E^f) \qquad 4.9$$

This rearrangement gives

$$E_{eq} = E^f + \frac{RT}{nF} \ln \frac{C_{Ox}}{C_R} \qquad 4.10$$

This is the Nernst equation. Thus the kinetic treatment correctly leads to the thermodynamic expression 4.10 under equilibrium conditions.

Using equations **4.6**, **4.8** and **4.10** a relation between i_0 and k_h^o can be obtained

$$i_o = nFAk_h^o \cdot C_{Ox}^{(1-\beta)} \cdot C_R^\beta \qquad \text{4.11}$$

Now, dividing equation 4.7 by equation 4.11 and rearranging the resulting equation using equation 4.10 the most general expression for electron transfer (equation 4.12) obtained is

$$i = i_o \left\{ \frac{C_{Ox}(o,t)}{C_{Ox}} \exp(-\beta\, nf\,\eta) - \frac{C_R(o,t)}{C_R} \right\} \{\exp[(1-\beta)\, nf\,\eta]\}$$

$$\text{4.12}$$

In this expression η is the overvoltage and is defined as $(E - E_{eq})$.

Several simplifications to the above general expression are possible. For example, in steady state polarization measurements using higher concentrations of Ox as well as R, it may be assumed that the surface concentrations of Ox and R are equal to their bulk concentrations respectively. Under these conditions, the more popular Butler-Volmer equation is obtained from equation 4.12.

$$i = i_o \{\exp(-\beta\, nf\,\eta) - \exp[(1-\beta)\, nf\,\eta]\} \qquad \text{4.13}$$

Two further simplifications of equation **4.13** are possible. If $|\eta| \gg 120$ mV one of the terms in equation 4.13 would become negligible when compared with the other term. For example, if $\eta < -120$ mV, the first term becomes very much larger than the second term and so

$$i = i_o \exp(-\beta\, nf\,\eta) \qquad \text{4.14}$$

and

$$\eta = \frac{2.303\, RT}{\beta\, nf} \log i_o - \frac{2.303\, RT}{nF} \log i \qquad \text{4.15}$$

This expression is popularly known as the Tafel expression.

Another simplification of equation 4.13 is possible under the low field approximation $|\eta| \leqslant 10$ mV. Under these conditions, the exponential term in equation 4.13 may be linearized and one obtains

$$i = -\frac{i_o \cdot nF\eta}{RT} \qquad \text{4.16}$$

or

$$\frac{\eta}{i} = -\frac{RT}{nF\,i_o} \qquad\qquad 4.17$$

The value η/i, in equation 4.17 is also called the charge transfer resistance.

Also consider one more simplification to the general expression in equation 4.12. When i_o is much greater than i, the value $i/i_o \ll 1$. In the limiting conditions, one may assume $i/i_o \simeq 0$ and equation 4.12 then gives

$$\frac{C_{Ox}\,(o,\,t)}{C_{Ox}}\,\exp\,(-\beta\,nf\,\eta) = \frac{C_R\,(o,\,t)}{C_R}\,\exp\,\{(1-\beta)\,nf\,\eta\} \qquad 4.18$$

Using equation 4.7 for C_{Ox}/C_R in this expression, we obtain

$$E = E^o + \frac{RT}{nF}\,\ln\,\frac{C_{Ox}\,(o,\,t)}{C_R\,(o,\,t)} \qquad\qquad 4.19$$

This is the surface boundary condition we employed for LSV and CV solutions of Fick's law of diffusion in Chapter 3. The present derivation clearly indicates the validity of equation 4.19 whenever i_o values or k_h^o values are very high.

The equations derived so far in this section are the building blocks of electrochemistry. The terms involved, their meaning and the quantitative expressions defining them must be understood properly. It is for this reason that all these expressions have briefly but systematically been derived here. More detailed derivations may be found in all the books dealing with electrode kinetics [11–15].

However, it is still true that the voltammetric behaviour of a single step process is controlled completely by two parameters k_h^o and β and equation 4.7 is the only expression generally employed as boundary condition for LSV and CV solution. This equation also contains n and E^f whose significance has been considered earlier (Chapter 3).

In dealing with electrode kinetics, two extreme conditions are usually considered. For quasireversible processes (Sec. 4.3.2) the k_h^o values are high and current would be noticed even for small values of $|\,E - E^f\,|$. Hence, the complete equation 4.7 must be used as a boundary condition. In the other extreme situation when k_h^o values are very small, the current would increase only when $|\,E - E^f\,|$ values are very high. When this is the case, one of the terms in

equation 4.7 may be neglected. For example, when one deals with reduction (highly negative E value), the above equation may be approximated to

$$i = nFAk_h^o \, C_{Ox}(o, t) \, \exp \{-\beta \, nf \, (E - E^f)\} \qquad 4.20$$

This is the boundary condition employed for LSV solution of irreversible charge transfer (Section 4.3.1).

4.2.2   MULTISTEP CHARGE TRANSFER

In the above section, charge transfer kinetics have been treated as a single-step process involving n electrons. However, statistically it is highly unlikely that more than one electron will be transferred to one Ox species at a time, which would amount to three or four body interaction. Hence one must assume that in the electrochemical kinetics only one electron transfer should take place in each step. If this is so, how does one handle multiple electron transfer?

If n electron transfers take place at different potential regions, then one can handle each step in the charge transfer kinetics as a separate process. Suppose there are two one-electron transfer steps

$$A + e \underset{k_{b,1}}{\overset{k_{f,1}}{\rightleftharpoons}} A^{\cdot -} \qquad 4.21$$

$$A^{\cdot -} + A + e \underset{k_{b,2}}{\overset{k_{f,2}}{\rightleftharpoons}} A_2^{2-} \qquad 4.22$$

If E^f values for these processes are different and both the processes are slow, one can define $k_{h,1}^o$ and $k_{h,2}^o$ for the separate steps and apply the theory developed above (Sec. 4.2.1) for each step.

But if both the charge transfer steps take place around the same E^f value and only a single LSV or CV wave is noticed, how does one treat the problem? Again, one resorts to the same methods adopted in multistep chemical process studies. Two methods may be generally employed based on a steady state assumption and quasi-equilibrium assumption. Steady state assumption would be a better choice when the rate constants of both the processes are of the same magnitude

and measurable under limiting conditions. However, in electro-chemical kinetics one rarely encounters such a situation [11–15]. Hence this study shall be confined to a brief consideration of quasi-equilibrium treatment. One assumes that mass transfer effects are absent, that is, the surface and bulk concentrations are equal for all species considered. Basically, in this treatment, it is assumed that in a multistep process, one step is very much slower than all the other steps (Fig. 4.1). Hence one considers that all the steps other than the slowest step are at quasi-equilibrium at each applied
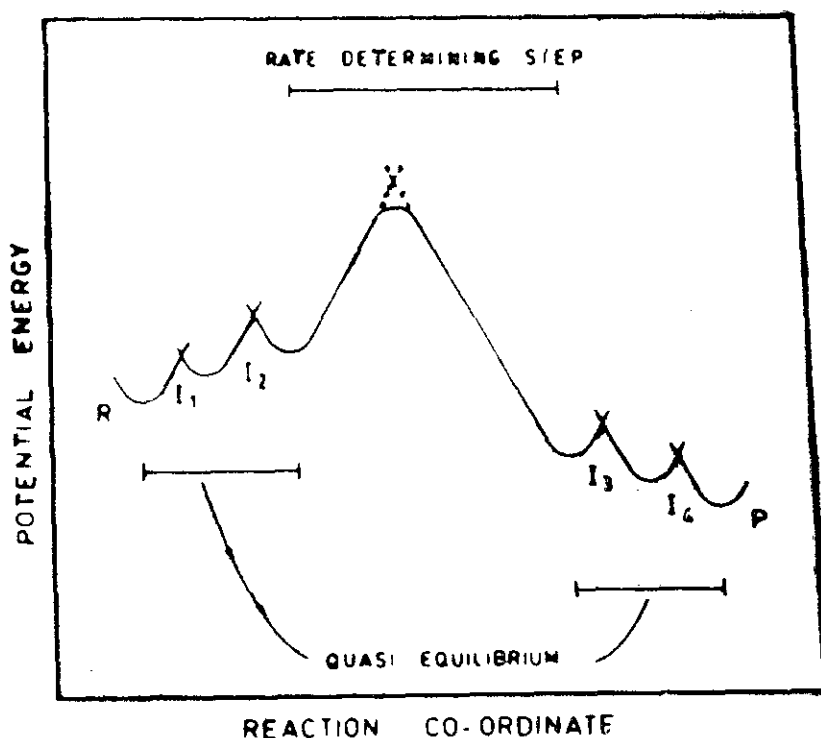

Fig. 4.1 Potential energy-reaction coordinate diagram for a multistep chemical process R—reactant; I_1, I_2, I_3, I_4—intermediate; P—product.

potential E. The slowest step in the sequence is called the rate-determining step or briefly *rds*. Consider for example equations 4.21 and 4.22; if the rate constants of equation 4.21 are much smaller than those of equation 4.22 one can assume that the second electron transfer step is in quasi-equilibrium. The rate of the overall reduction process will then be controlled by equation 4.21.

$$v = nfAk^o_{f,1} \cdot C_A \cdot \exp(-\beta f E) \qquad 4.23$$

under totally irreversible charge transfer conditions. Hence the E versus log i plot will have a slope of 2.303 $RT/\beta F$ as in equation 4.15.

However if equation 4.22 is rate controlling, the equation one gets is

$$v = k^o_{f,2} \cdot C_A \cdot C_{A^-} \exp(-\beta fE) \qquad 4.24$$

The concentration term C_{A^-} in equation 4.24 is not known. This can however be calculated if one assumes that equation 4.21 is in equilibrium at any potential E. We then get

$$k^o_{f,1} C_A \exp(-\beta fE) = k^o_{b,1} C_{A^-} \exp\{(1-\beta)fE\} \qquad 4.25$$

Therefore, the equation will be

$$C_A = \frac{k^o_{f,1}}{k^o_{b,1}} C_A \cdot \exp(-fE). \qquad 4.26$$

Substituting the value of C_{A^-} from equation 4.26 in equation 4.24, the equation becomes

$$v = \frac{k^0_{f,1}}{k^0_{b,1}} \cdot k^0_{f,2} C^2_A \exp\{-(1+\beta)fE\} \qquad 4.27$$

Now carefully compare equation 4.23 and equation 4.27, which are the rate expressions for equations 4.21 and 4.22 as *rds* respectively; one can notice two means of distinguishing them, namely

$$\left(\frac{d \log i}{d \log C_A}\right)_E = 1 \qquad 4.28$$

and

$$\left(\frac{dE}{d \log i}\right)_{C_A} = \frac{-2.303RT}{\beta F} \qquad 4.29$$

from equation 4.23 for equation 4.21 as the *rds*. On the other hand

$$\left(\frac{d \log i}{d \log c}\right)_E = 2 \qquad 4.29$$

and

$$\left(\frac{dE}{d \log i}\right)_{C_A} = \frac{-2.303 \, RT}{(1+\beta)F} \qquad 4.30$$

from equation 4.27 for equation 4.23 as *rds*. The term $(d \log i/d \log C_A)_E$ is the reaction order of the electrochemical reactions. The term $(dE/d \log i)_{C_A}$ is the Tafel slope for the electrochemical reactions. It is evident that by measuring these two

parameters one can easily distinguish between these two mechanistic possibilities.

The product A_2 can also be formed by another route. After equation 4.21 a dimerization process can take place:

$$2A^- \underset{k_{b,3}}{\overset{k_{f,3}}{\rightleftharpoons}} A_2^{2-} \qquad 4.31$$

The rate expression for this purely chemical reaction is

$$v = k_{f,3} \cdot C_{A^-}^2 \qquad 4.32$$

The value of C_{A^-} can again be substituted from equation 4.27

$$v = \left(\frac{k_{f,1}}{k_{b,1}}\right)^2 k_{f,3} C_A^2 \exp\ (-2fE) \qquad 4.33$$

The reaction order for this mechanism is 2 and Tafel slope is $2.303RT/2F$ as noted from this expression.

There is one more difference between mechanism involving reactions 4.21, 4.22 scheme discussed earlier and the mechanism involving 4.21, 4.31 scheme considered above (equation 4.33). In the former sequence, the *rds* would occur only once for the overall reaction $2A^- \rightarrow A_2^{2-}$. In the latter sequence, the *rds* must occur twice. This distinguishing parameter is defined as the stoichiometric number v. Stoichiometric number may be defined as the number of times of occurrence of *rds* for the occurrence of one complete overall process. In the example of two-step one-electron process considered above, it is noted that three possible mechanisms exist (Table 4.1). The number of possible mechanisms would still increase if the overall process involves say four electrons. For example, oxygen evolution from OH^- which is a four electron process has 17 possible reaction mechanisms [16]. These mechanisms may be distinguished by the careful evaluation of Tafel slopes, reaction orders and the stoichiometric numbers [16].

Finally consider the generalized current-potential expression describing the multistep electrochemical kinetics. One can, in fact, derive the overall current-potential expression for a multistep process which is very similar to equation 4.13 derived for a single step process [17].

$$i = i_o \left\{\exp\ (-\alpha_c n_a f \eta) - \exp\ (\alpha_a n_a f \eta)\right\} \qquad 4.34$$

The similarity between equations 4.13 and 4.34 must not lead to

Table 4.1

Mechanistic pathways for an overall two—electron two—step process

Mechanism	$dE/d \log i$ (mV)
(i) $A + e \rightarrow A^{\cdot -}$ $A^{\cdot -} + A^{\cdot -} \rightleftharpoons A_2^{2-}$	120
(ii) $A + e \rightleftharpoons A^{\cdot -}$ $A^{\cdot -} + e \rightarrow A^{2-}$	40
(iii) $A + e \rightleftharpoons A^{\cdot -}$ $A^{\cdot -} + A + e \rightarrow A_2^{2-}$	40
(iv) $2A + 2e \rightleftharpoons 2A^{\cdot -}$ $2A^{\cdot -} \rightarrow A_2^{2-}$	30

($A^{\cdot -}$ indicates unstable ion radical)

the conclusion that both are identical. The i_o value for the multistep process, for example, has a number of quasi-equilibrium rate constants or equilibrium constants (see equations 4.27 and 4.33 for example), the rate constant for the *rds* and the concentrations and reaction orders of the reactants and products involved [11-15]. The i_o value cannot thus be used to calculate the heterogeneous electron transfer rate constant of the *rds* involved as one can in the case of a single step process be using equation 4.11. Another difference is that instead of n in the exponential of the single step process, there is n_a, the number of electrons involved in the activation step in a multistep process (equation 4.34).

Another, even more important, difference between equation 4.13 and equation 4.34 is that in the expression for electron transfer, there are the cathodic transfer coefficient (α_c) and the anodic transfer coefficient (α_a) instead of the symmetry factor noted in the single step process. This fact is often missed by many and misunderstood by many more, leading to a lot of confusion in the literature. In a single step process, the Tafel slope at 25°C, for example, is equal to $59/\beta n$ mV according to equation 4.15. Since β, the symmetry factor, is generally 0.5 [18] (see Sec. 4.4.2), the Tafel slope value can be used to evaluate n, the total number of electrons involved in the

process. This method is not applicable in the multistep process. α_c and α_a values cannot be taken to be 0.5. Their values, in fact, depend on the total number of electrons involved in the overall process (n), total number of electrons transferred before the *rds* (n_b), number of electrons involved in the *rds* (n_a), stoichiometric number (ν) and symmetry factor (β) and are given by

$$\alpha_c = \frac{n_b}{\nu} + n_a \beta \qquad\qquad 4.35$$

$$\alpha_a = \frac{n - n_b}{\nu} - n_a \beta \qquad\qquad 4.36$$

In a multistep process, n may be obtained from product analysis or coulometric studies. If n is known, α_c and α_a can be obtained from experimental Tafel slope measurements. The stoichiometric number may be obtained by adding equations 4.35 and 4.36 which gives

$$\alpha_c + \alpha_a = \frac{n}{\nu} \qquad\qquad 4.37$$

The symmetry factor is usually assumed to be 0.5. The exact mechanism involved can then be established by making the theoretically predicted α_c and α_a values (by guessing the right sequence that gives correct n_b and n_a values) with those obtained experimentally.

The above expressions for transfer coefficients are, however, valid only when the intermediates such as A^- are not adsorbed on the electrode surface or when the surface coverage by the adsorbed species is extremely low. Such situations arise, for example, when organic reactions are studied in aprotic media. The transfer coefficients would vary substantially when intermediate adsorptions are involved. These variations are in fact employed to establish intermediate adsorption (Chapter 12).
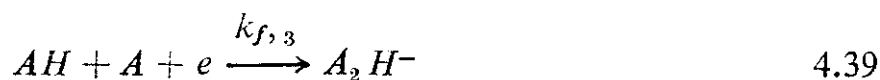
The similarity in form noted between equation 4.13 and equation 4.34 for single step and multistep electron transfer, however, is very important from the analytical point of view. Hence, although no explicit mathematical treatment of LSV and CV techniques for multistep processes are available, it is noticed that these techniques are generally employed for multistep processes as well (Section 4.4.3). Of course, the methods developed for the evaluation of k_h^0

for single step processes cannot be used for estimating the k_h^o of the *rds* of a multistep process. (The authors for that matter are not aware of any other experimental method that can evaluate the k_h^o of the *rds* of such multistep processes. Only the overall rate i_o at the equilibrium potential are experimentally accessible). However, the experimental expressions for the evaluation of Tafel parameters are applicable for both single step and multistep processes and hence LSV and CV techniques may also be used for evaluating transfer coefficients and reaction mechanisms.

4.2.3 INFLUENCE OF CHEMICAL EQUILIBRIUM ON CHARGE TRANSFER KINETICS

In this section (Section 4.2) we have so far discussed the electrochemical and chemical processes (equation 4.31) of electroactive molecules alone. However, a number of chemical processes can interfere in the kinetics of electrochemical processes as well as in the case of thermodynamics of electrochemical processes discussed earlier (Chapter 3).

Instead of the sequence in equations 4.21 and 4.22 consider the sequence involving, for example, an intermediate protonation step

$$A + e \underset{k_{b,1}}{\overset{k_{f,1}}{\rightleftharpoons}} A^{\bar{\cdot}} \qquad\qquad 4.21$$

$$A^{\bar{\cdot}} + H^+ \underset{k_{b,2}}{\overset{k_{f,2}}{\rightleftharpoons}} AH \qquad\qquad 4.38$$

$$AH + A + e \overset{k_{f,3}}{\longrightarrow} A_2 H^- \qquad\qquad 4.39$$

If equation 4.39 is considered to be the *rds*, one can write the rate expression for the irreversible charge transfer equation 4.39 as

$$v = k_{f,3}^o \, C_{AH} \cdot C_A \exp{(-\beta f E)} \qquad\qquad 4.40$$

The C_{AH} term may be obtained by assuming quasi-reversible equilibrium for the chemical reaction equation 4.38. Of course, this equilibrium is independent of potential.

$$k_{f,2} \cdot C_{A^-} \cdot C_H{}^+ = k_{b,2} \cdot C_{AH} \qquad 4.41$$

Therefore,

$$C_{AH} = \frac{k_{f,2}}{k_{b,2}} C_{A^-} \cdot C_{H+} \qquad 4.42$$

The concentration term C_{A^-} can be obtained from the quasi-equilibrium assumption of equation 4.21. We have already derived this expression (equation 4.26). Hence equation 4.42 now becomes

$$C_{AH} = \frac{k_{f,2}^o}{k_{b,2}^o} \cdot \frac{k_{f,1}^o}{k_{b,1}^o} \cdot C_{H+} \cdot C_A \cdot \exp(-fE) \qquad 4.43$$

Now, substituting this value for C_{AH} in equation 4.40, what is obtained is

$$v = k_{f,3}^o \cdot \frac{k_{f,2}^o}{k_{b,2}^o} \cdot \frac{k_{f,1}^o}{k_{b,1}^o} \cdot C_A^2 \cdot C_{H+} \exp\{-(1+\beta)fE\} \qquad 4.44$$

Hence the reaction scheme involving equations 4.21, 4.38 and 4.39 gives a Tafel slope of $59/(1+\beta)$ mV at 25°C and the reaction order $r_A = 2$ and $r_{H+} = 1$.

It would be illustrative to compare equation 4.44 involving intermittent chemical equilibrium with equation 4.27 which is for the scheme that does not involve the chemical equilibrium. The Tafel . slope is not affected by the chemical reactions. They only exhibit themselves in the reaction orders.

Hence one can generalize that the chemical equilibrium associated with charge transfer kinetics interferes only with the reaction order. A variety of such chemical equilibrium processes such as acid-base equilibria (which, of course, is most extensively studied) and complex formation equilibria may influence charge transfer kinetics. By carefully evaluating the reaction order with respect to the suspected species at constant electroactive species concentration and potential, one may arrive at the correct mechanism. In employing electroanalytical techniques for such studies, one must ensure that the current values are devoid of mass transfer effects (Section 4.4.3).

In the discussions on chemical equilibrium with reversible charge transfer (Section 3.2.2) one relied more on the potential values and their variation with concentration of the chemical reactant (such

as H^+) to extract information on chemical equilibrium. One also noticed there that the equilibrium parameters such as K values could be obtained from such studies. In this section, it is advocated that one must rely on current measurements primarily for evaluating chemical equilibrium effects. Why ?

In the reversible charge transfer processes, the E_p measurements, for example, directly gave us the thermodynamic information. This is not the case in the irreversible charge transfer. E_p value depends on the kinetics of charge transfer. Extracting the equilibrium parameters of chemical reaction from E_p measurements must therefore be quite difficult, if not impossible. One must first evaluate all charge transfer parameters (k_h^o, n, E_n) in the absence of chemical interaction. One must also ensure that chemical interactions influence only E^f and not other kinetic parameters. (There is no easy means for doing this, of course). If these tasks are accomplished, then the chemical reactions may be evaluated by potential measurements. All these discussions, however, apply to the single step process only. Multistep reactions are even more difficult to be evaluated by this method.

4.2.4   THE MASS TRANSPORT

As far as the mass transport characteristics are concerned, the basic Fick's expressions do not depend on whether the charge transfer process is reversible or irreversible. For the single step process equation 4.1 which is the same as equation 3.1, the linear diffusion expressions under stationary conditions are the same expressions represented by equations 3.28 and 3.29. All the five boundary condition equations 3.30 to 3.34 are also applicable. It is only in the boundary condition at the surface which relates the current and potential with surface concentrations C_{ox} and C_R that the two processes differ. When the kinetics of charge transfer is slow, boundary condition equation 3.27 is no longer applicable.

Depending on whether the k_h^o value is small or large, equations 4.20 and 4.7 respectively are employed for the final boundary condition. Instead of β n in these expressions, αn_a in these expressions are employed. For single step process, of course, αn_a becomes β n (Sections 4.3.1 and 4.3.2). Hence in the following LSV and CV treatments, equation 4.45 is employed for describing irreversible

charge transfer (Sections 4.3.1 and 4.3.2) and equation 4.46 for quasi-reversible charge transfer analysis.

$$i = nFA \, k_h^o \, C_{ox}(o, t) \exp \{-\alpha n_a f (E - E^f)\} \qquad 4.45$$

$$i = nFAk_h^o[C_{ox}(o, t) \exp \{-\alpha n_a f (E - E^f)\}$$

$$-C_R(o, t) \exp \{1 - \alpha)n_a f(E - E^f)\}] \qquad 4.46$$

Thus, in addition to D, n, E^f that controlled voltammetric behaviour of reversible charge transfer, there is k_h^o, α and n_a that control the voltammetric behaviour of charge transfer kinetics.

4.3. THE METHOD

4.3.1. IRREVERSIBLE CHARGE TRANSFER

a) LSV and CV methods

When k_h^o value is sufficiently small (for a quantitative range, see Sec. 4.3.2), one can employ equation 4.45 as the boundary condition for solving the Fick's diffusion equations. The first solution of this problem was given by Delahay [19] in 1953. Reinmuth, in a series of papers, analysed the LSV and CV behaviour in greater detail [20]. Complete numerical solutions were later presented by Nicholson and Shain [21].
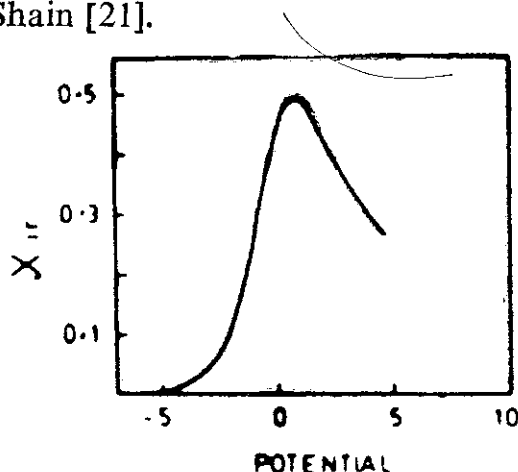

Fig, 4.2 Typical linear sweep voltammogram for totally irreversible charge transfer process.
$$X(E) = i/nFA \, C_{ox}D_{ox}^{1/2} \cdot (\alpha n_a Fv/RT)^{1/2}$$

A typical LSV curve for a totally irreversible charge transfer is presented in Fig. 4.2. The expressions for peak current (i_p), peak

potential (E_p) and peak width are given by the following equations :

$$i_p = 0.496 \, nFAC_{Ox}D_{Ox}^{1/2} \, v^{1/2} \left(\frac{\alpha n_a f}{RT}\right)^{1/2} \pi^{1/2} \qquad 4.\ 7$$

$$E_p = E^f - \frac{RT}{\alpha n_a F}\left\{0.780 + \ln \left(\frac{D_{Ox}}{k_h^o}\right)^{1/2} + \ln \left(\frac{\alpha n_a F v}{RT}\right)^{1/2}\right\} \qquad 4.48$$

$$E_p - E_{p/2} = \frac{1.857 \, RT}{n_a F} \, \text{mV} \qquad 4.49$$

The E values in equations 4.48 and 4.49 are in mV. The expressions at 25°C are presented in Table 4.2. Substituting the value of E_p from equation 4.48 in equation 4.47 one may also obtain another useful expression for i_p which contains the experimentally measurable E_p value and E^f in addition to k_h^o.

$$i_p = 0.227nFAk_h^o C_{Ox} \exp \{ - \alpha n_a f (E_p - E^f)\} \qquad 4.50$$

Table 4.2

Voltammetric characteristics of irreversible charge transfer

$$O_x + ne \rightarrow R$$

$i_p = 2.99 \times 10^5 \times n \, (\alpha \, n_a)^{1/2} . AC_{Ox} D_{Ox}^{1/2} . v^{1/2}$	4.2a
$E_p = E^f + \dfrac{0.059}{\alpha n_a} \left[1.796 + \log \left(\dfrac{D_{Ox}^{1/2}}{k_h^o}\right) + \log (38.92 \times n_a v)^{1/2} \right]$	4.2b
$E_p - E_{p/2} = - \dfrac{47.7}{\alpha \, n_a} \, \text{mV}$	4.2c
$dE_p/d \log v = \dfrac{-30}{\alpha n_a} \, \text{mV}$	4.2d
$i_p = 0.227 \, nFAC_{Ox} \cdot \exp \{ - \alpha n_a f (E_p - E^f)\}$	4.2e

In equations 4.2.a and 4.2.e, i_p is in amp, A is in cm^2, C_{Ox} is in moles/cm^3, D_{Ox} is in cm^2/sec and v is in Volt/sec.

Now it would be worthwhile considering the implications of LSV behaviour of a totally irreversible wave (Table 4.2). The peak

current term (4.2.a) now contains the kinetic parameter (αn_a) in addition to n and D_{ox} found in i_p expression of a reversible process (Table 3.2). The i_p current, however, is still proportional to $v^{1/2}$ and C_{ox} as in the case of a reversible process.

The peak potential expression (4.2.b) however contains even more significant differences. The E_p value now is a function of D_{ox}, k_h^o, αn_a as well as the sweep rate v. Thus the E_p measurement of an irreversible charge transfer process cannot be used to measure E^F value as was done in the reversible case. As the k_h^o value decreases, the E_p shifts to a more and more cathodic potential. One may derive another useful relation from equation 4.48 which is useful for evaluating αn_a.

$$\frac{dE_p}{d \log v} = \frac{1.15\,RT}{\alpha n_a F}$$ 4.51

This equation (4.2.d at 25°C) as well as (4.2.c) may be experimentally verified. If both these expressions are obeyed over as wide a sweep rate range as possible, then one may ascertain that the process is an irreversible charge transfer. Equations 4.2.c and 4.2.d may also be used to evaluate αn_a in such a situation. Now one can employ equation 4.2.a to evaluate n if D_{ox} is known and *vice versa*.

If E^f is known by some other experimental method (Section 4.3.2) one may evaluate k_h^o using equation 4.2.e. In the absence of proper E^f values, some attempts are usually made to evaluate k_h^o values assuming E^f as zero. This approach in LSV studies seems to have the origin from the polarographic studies of irreversible processes where k_f^o values represented by equation 4.4 are evaluated. It is worthwhile emphasizing here that k_h^o values are not identical to k_f^o values. Only k_h^o values have real kinetic significance. They directly indicate the charge exchange rate at the formal electrode potential of each reaction. k_f^o is the rate at some arbitrary potential. Its value depends on the reference scale used For redox reactions whose E^f values are very negative, k_f^o values of 10^{-20} cm/sec and less are obtained. No meaningful information is found from such measured 'rate constants'. Such attempts often confuse the electrode kinetic studies rather than produce any useful additional information.

However, when E' values are not known, one may get an approximate estimate of k_h^o (again if it is certainly a single step process) by the following expression

$$i = nFAk_h{}^oC_{ox} \exp\{ -\alpha n_a f (E - E_i)\} \qquad 4.52$$

This equation suggested by Reinmuth [20] is applicable when $i <$ 10 per cent of i_p, that is, at the foot of the irreversible CV wave [21]. The accurate estimation of E_i, the potential at which the faradaic process starts, is the basic criterion that determines the accuracy of k_h^o evaluated by this method.

The peak current expressions discussed above apply when linear diffusion prevails. Corrections for spherical diffusion effects in HMDE have also been worked out [22]. Numerical tabulations for such corrections are also available [21]. However, as in the case of reversible charge transfer, as the radius increases, these correction effects are minimized.

So far discussions have been confined to LSV behaviour. In the CV curves, one would not notice any anodic peak in the reverse direction for a totally irreversible charge transfer. Hence the peak current ratio $i_{p,a}/i_{p,c}$ will be zero under these conditions. CV studies in such cases can only offer a qualitative support to the fact that the charge transfer is irreversible. No quantitative evaluation of charge transfer kinetics is possible from such studies.

The CV curve of a reversible charge transfer followed by fast irreversible chemical reaction (EC_{irr} scheme) is very similar qualitatively to an irreversible CV curve discussed above. There are, however, quantitative means to distinguish them (Chapter 5). This point is mentioned here because whenever an irreversible CV wave is noticed, an attempt should be made to distinguish between these two possibilities. For example, a number of organic electrode processes in aprotic media must invariably involve fast charge transfer. The CV waves are irreversible because of the reactivity of the radical anions or cations formed during electron transfer. Such chemical follow-up reactions have been very well-documented in literature (Chapter 5). But still one can easily find reports in recent literature which employ the equations described here for such processes and evaluate charge transfer rate parameters for them.

b) Convolution sweep voltammetry

It has been established earlier (Section 3.3.1) that one can express the surface concentration $C_{ox}(o, t)$ by a semi-integral or convolution integral (equation 3.51) where I is the integral given by equation 3.48. These expressions were derived employing the common boundary conditions for the reversible as well as irreversible charge transfer. Hence these equations are also applicable to irreversible charge transfer. Substituting the value of $C_{ox}(o, t)$ from equation 3.51 in equation 4.45, one gets

$$i(t) = \frac{k_h^o}{D_{ox}^{1/2}} (I_l - I) \exp \{ - \alpha\, n_a f (E - E^f)\} \qquad 4.53$$

$$E = E^f - \frac{RT}{\alpha\, n_a F} \ln \left[\frac{D_{ox}^{1/2}}{k_h^o} \right] - \frac{RT}{\alpha\, n_a F} \ln \left[\frac{i(t)}{I_l - I} \right] \qquad 4.54$$

From E versus $\ln [i(t)/(I_l - I)]$ plots, one may obtain the transfer coefficient αn_a. If E^f is known, k_h^o value can then be calculated. The kinetic analysis of data in this method is very similar to the analysis of polarographic data [23, 24]. The only problem, of course, is to obtain I, the convoluted integral at different time intervals. A number of mathematical techniques [25, 26] is, however, available for this purpose.

One important advantage of convolution integral analysis over LSV for irreversible charge transfer is that the limiting value I_l is not dependent on time or any other kinetic parameter such as (αn_a). I_l is simply given by

$$I_l = nFAD_{ox}^{1/2} \cdot C_{ox} \qquad 4.55$$

This is true irrespective of the nature of charge transfer [27, 28]. Hence, the same expression may be used for all charge transfer processes that are controlled by mass transfer. For LSV however, different expressions are used for i_p of a reversible. (Table 3.2) and an irreversible process. For quasi-reversible systems, the expressions are even more involved as we will see shortly (Section 4.3.2)

The semi-integral I can further be differentiated with respect to time. Such semi-differential analysis also has been carried out for irreversible charge transfer [29, 30].

4.3.2. QUASI-REVERSIBLE CHARGE TRANSFER

a) Linear sweep voltammetry

The first LSV solution of quasi-reversible charge transfer involving linear diffusion with equation 4.46 as the boundary condition was treated in an extensive work by Matsuda and Ayabe[31]. The peak current and peak potential expressions for such a process are much more involved. We shall, however, try to understand the voltammetric behaviour in a qualitative fashion. These authors probably employed a dimensionless parameter for the first time in LSV simulations.

$$\Lambda = \frac{k_h^o}{(D_{ox} \cdot nf\, v)^{1/2}} \qquad\qquad 4.55$$

A simple dimensional analysis would indicate that Λ is a dimensionless parameter. Its value is a measure of the rate constant of charge transfer (k_h^o) and the rate constant of mass transfer (or mass transfer coefficient). The LSV behaviour for a quasi-reversible charge transfer would depend on Λ and the transfer coefficient (αn_a). (Throughout the kinetic analysis, one encounters a number of such dimensionless parameters).

Typical LSV curves for various values of Λ and α are presented in Fig. 4.3. It is clear from these figures that as Λ decreases (or equivalently k_h^o decreases or sweep rate increases) the LSV waves shift in the cathodic directions. (The function $\chi\,(E)$ in Fig. 4.3 is directly related to the current in LSV). The peak current value also decreases with Λ. The decrease is even more clearly noticed when α is small.

When Λ values are high, the peak current is proportional to $v^{1/2}$ and equation 3.2.a of a reversible process is obeyed. At very low Λ values again i_p is proportional to $v^{1/2}$ and now equation 4.2.a of a totally irreversible charge transfer is obeyed. In between these two extremes, i_p is not linearly related to $v^{1/2}$ (Fig. 4.4).

Similarly, the expression of E_p also changes from that of a reversible process (Table 3.2) to that of an irreversible process (Table 4.2). The peak width $E_p - E_{p/2}$ value also changes similarly[31].

It must thus be concluded that LSV treatment discussed above is the general treatment for process controlled by charge transfer
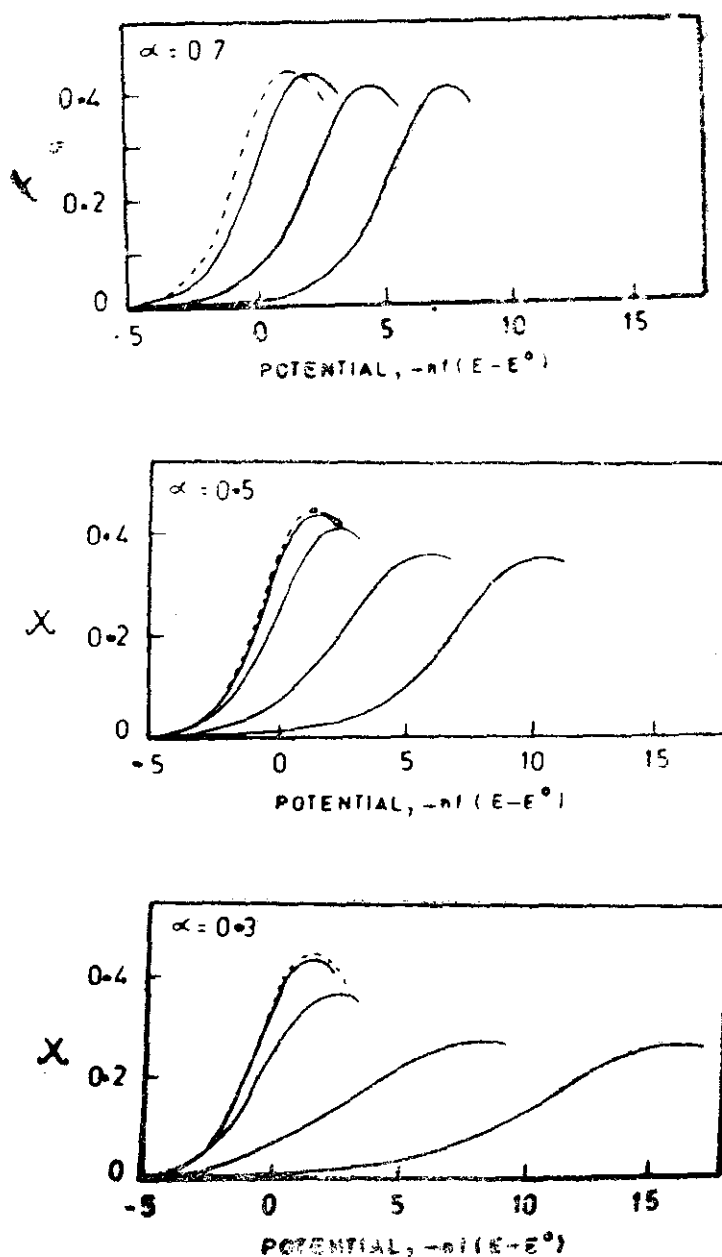
Fig. 4.3   Variation of quasi-reversible current function
for different values of α (0.7,0.5 and 0.3) as
indicated and the following values of Λ :
I. Λ = 10; II. Λ = 1; III. Λ = 0.1; IV. Λ = 0.01
(dashed curve is for a reversible reaction)

$$\chi(E) = i/nFAC_{ox} \, D^{1/2} \cdot (nFv/RT)^{1/2}$$

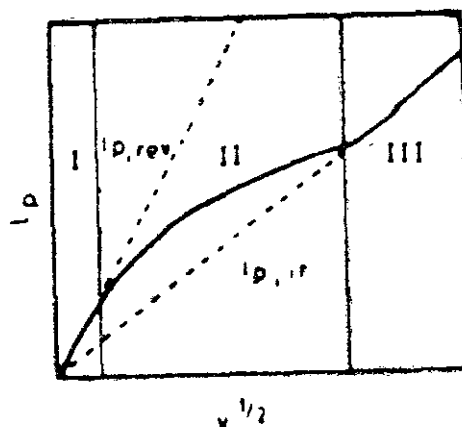[From H Matsuda and Y Ayabe, Z Elektrochem
59 (1955) 494].

Fig. 4.4   Dependence of peak current on the square root of sweep rate, [1—reversible region; 2—irreversible region. (From H Matsuda and Y Ayabe, Z Elektrochem 59 (1955) 494].

and linear diffusion. At one extreme (large Λ) this treatment leads to reversible LSV behaviour. At another extreme (small Λ) it leads to irreversible behaviour.

It would be useful to know the regions of k_h^o values where reversible, quasi-reversible and irreversible behaviour would be noted. For $n = 1$, $\alpha = 0.5$, $D = 10^{-5}$ cm^2/sec, $T = 25°C$ and $v = 1$ V/sec, these limits are as follows:

Reversible $\Lambda \geqslant 15$; $k_h^o \geqslant 0.3$ cm/sec

Quasi-reversible $15 \geqslant \Lambda \geqslant 10^{-2(1+\alpha)}$; $0.3 \geqslant k_h^o \geqslant 2 \times 10^{-5}$ cm/sec

Irrreversible $\Lambda \leqslant 10^{-2(1+\alpha)}$; $k_h^o \leqslant 2 \times 10^{-5}$ cm/sec

With the change of n, D, T and v, the range specified for k_h^o values would change but the range specified for Λ would not. We can, of course, calculate the range of k_h^o values under such conditions using equation 4.55. This indeed is the advantage of using such dimensionless parameters.

b)   Cyclic voltammetry

The CV solution for quasi-reversible charge transfer was developed in the early sixties [32, 33]. A number of quantitative treatments followed. The $i_p/i_{p,c}$ depends on k_h^o and α values. Typical CV curves of (a) reversible, (b) quasi-reversible, and (c) irreversible as presented in Fig. 4.5 are for comparison.

The most widely employed method in kinetic analysis of charge

transfer using CV measurements was reported by Nicholson [34] in 1965. He found that the peak potential separation $\Delta E_p = (E_{pa} - E_{pc})$ is a function of ψ which is further related to k_h^o by the following expression:

$$\psi = \frac{r^{\alpha/2}\, k_h^o}{(\pi\, D_{ox}\, nfv)^{1/2}} \qquad\qquad 4.56$$

where

$$r = (D_{ox}\,/\,D_R) \qquad\qquad 4.57$$

Hence, if one knows D_{ox}, D_R and n value of a redox couple, he can obtain ΔE_p experimentally and the corresponding ψ value from the Table 4.3 and hence calculate k_h^o. Even if both D_{ox} and D_R are not available, approximate value of k_h^o can still be determined by assuming $r = 1$. ψ actually depends slightly on α. The value of ψ functions in Table 4.3 are for $\alpha = 0.5$. ψ function in Table 4.3 also contain some extension work by Perone [35].

The simplicity and elegance of this method have been received widely. The usefulness and limitations of this method are discussed in Section 4.4.1.

Cyclic voltammetric solution for quasi-reversible charge transfer under convective diffusion (RDE voltammetry) have been recently worked out [36, 37]. However, this method is yet to find widespread applications.

c) *Convolution sweep voltammetry*

Surface concentration expressions for $C_{ox}\,(o,t)$ as well as $C_R\,(o,t)$ in terms of convolution integrals may easily be substituted in equation 4.46. This would directly give the convolution integral-potential relationship. The mechanistic as well as analytical implications of the resulting expressions have been extensively considered [23-30]. The limiting value of convolution integral is again given by equation 4.55. Hence the integral is independent of the rate of charge transfer. This is extremely useful from an analytical point of view, especially in a quasi-reversible region since the peak current of LSV has no simple analytical solution here (Fig. 4.5).

Another interesting application of CSV in mechanistic analysis was pointed out by Saveant and co-workers [23, 24, 38]. One can evaluate the charge transfer rate constant which depends on potential, without assuming the applicability of Butler-Volmer equation or equation 4.46. Equation 4.46 basically asumes that $\alpha\, n_a$ term is independent of potential [4-6]. Recent theories of electron transfer predicts
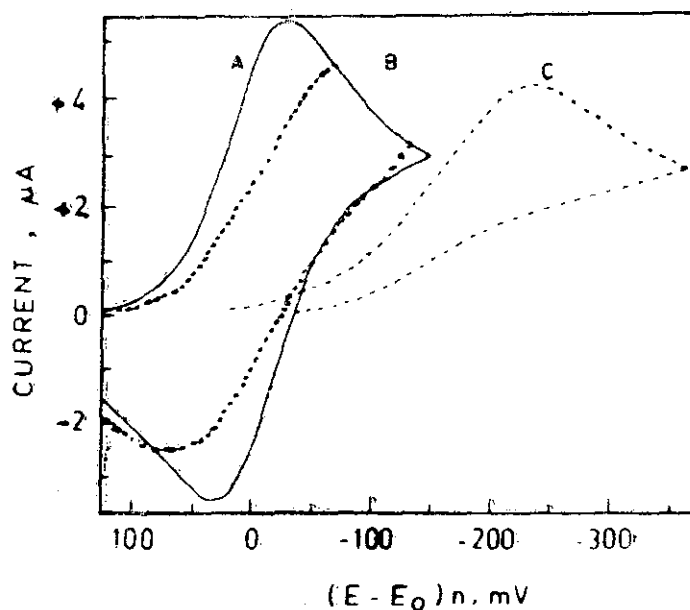
Fig. 4.5   Typical cyclic voltammetric curves, $E^o = 0$.
A – Totally reversible process
B – Quasi-reversible process
C – Irreversible process

that α must depend on potential [7 8]. It would be better to evaluate k_f (or k_b) in equation 4.2 as a function of potential experimentally and find out if $d \ln k_f/dE$ has a finite slope or not. Taking the relationship between E^o and K or k_f/k_b, one can write equation 4.2 in the following form [23, 24, 38].

$$i = n\,FA\,k_f\,[C_{ox}(o,\ t)-C_R(o,\ t)\exp\{-n_f(E-E^f)\}]\qquad 4.58$$

Now substituting the value of $C_{ox}\,(o,t)$ and $C_R\,(o,t)$ equation obtained is

$$\ln k_f(E) = \ln D_{ox}^{1/2}-\ln\left[I_l-\frac{I}{i}\left\{1+\exp nf\,(E-E_{1/2})\right\}\right]$$

The limiting expressions for reversible as well as irreversible charge transfer may also be obtained from this expression [24, 38].

Typical CV and corresponding CSV curves for a quasi-reversible process are presented in Fig. 4.6. A method for obtaining $E_{1/2}$ (or $\simeq E^f$) for a quasi-reversible process also is presented in this figure. In the CV curve, one can determine the point where $i = 0$. The convolution integral at this point is $I_{i=0}$ and the potential may be denoted as $E_{i=0}$. Since $k_f\,(E)$ has a finite value at this potential as well,
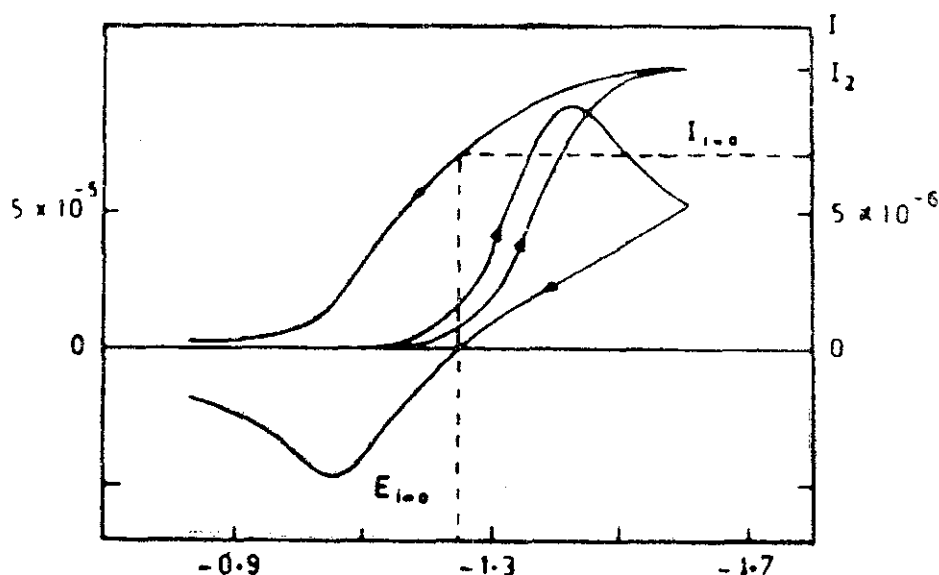
Fig. 4.6   Experimental cyclic voltammogram and its convolution of 0.5 mM tert. nitrobutane in DMF containing 0.1 M tetra-butyl ammonium iodide. $v = 17.9$ V/sec. Dotted line illustrates the method of derermining $E_{i=0}$ and $I_{i=0}$ [From JM Saveant and D Tessier, J Electroanal Chem 65 (1975) 57].

from equation 4.59 one notices that the numerator of the second term on the right hand side must be zero. Hence

$$E_{1/2} = E_{i=0} - \frac{RT}{nF} \ln \left[\frac{I_l - I_{i=0}}{I_{i=0}} \right]$$

Knowing $E_{1/2}$ from the method one can proceed to calculate $k_f(E)$ knowing all other parameters.

The CSV technique is a very useful one for a detailed evaluation of charge transfer kinetics. The solution resistance compensation as well as double layer corrections can also be easily applied [24]. However, this method has not been used widely probably because of the requirements of numerical acquisition of data and their semi-integration. With the entry of computers in the laboratories, the situation may change in the near future.

4.4   THE PROCESS

4.4.1   THE HETEROGENEOUS RATE CONSTANT

If both O_x and R are stable in the solution; if the charge transfer rate constants are also sufficiently slow; and if one can prepare

solutions with high concentrations of C_{ox} and C_R, steady state polarization technique is the best for measuring k_h^o values. Then equation 4.14 is obeyed over a wide potential region in the cathodic as well as anodic regions. By $\eta - \log i$ plots obtained in the cathodic and anodic regions, i_o, n_a, and E^o values can be obtained [11–15]. The kinetic parameters obtained for such processes have also been tabulated [39]. For detailed descriptions of experimental work of this kind, one may specifically refer to Veter's work [13].

Transient techniques are required for k_h^o evaluation, when one or more of the conditions set above are not fulfilled. If O_x or R is not stable in the medium over long periods, their kinetics must be evaluated within the short life span of the species. If k_h^o values are sufficiently large, steady state methods would give only Nernstien behaviour. At very low eoncentrations, a well-defined mass transfer control is needed to obtain kinetic information from the total response due to mass transfer and kinetics. LSV and CV methods are the easiest transient methods available for kinetic analysis. A quick preliminary study by CV is almost always required before employing other transient techniques such as faradaic impedance [40], chrono-coulometric [41] or galvanostatic double pulse techniques [42]. With improvements in cell design, data acquisition and analysis (Chapter 2) CV can be used to evaluate the rate constant of almost all electron transfer processes known. Kinetic parameters obtained by transient and steady state techniques have been tabulated [43]. However, a great deal of new data are now available which are yet to be collected.

Irreversible charge transfer may be easily characterized using equations presented in Table 4.2 i_p would be proportional to $v^{1/2}$. But E_p would shift cathodically with sweep rate. E_p versus $\log v$ would give a straight line. $E_p - E_{p/2}$ also would give a constant value. However, all these properties would be exhibited by EC_{irr} reaction (Section 4.31 and Chapter 5). The following properties may be used to distinguish between the two possibilities (E_{irr} versus $E_r C_{irr}$). If the reverse wave is noticed very near the cathodic wave (even if the wave height is very small) on the reverse scan as the sweep rate is increased, $E_r C_{irr}$ mechanism probably operates. Then at very high sweep rates, one can completely characterize E_r process. If the reverse wave is noticed at substantially anodic potentials ($\Delta E_p > 400$ mV), the E_{irr} process may be presumed. Quantitatively

$E_p - E_{p/2}$ for E_{irr} would be around 95 mV for a single step one electron E_{irr} process according to equation 4.2.c in Table 4.2. For EC_{irr} process this value would be $56/n$ mV and hence equal to or less than this value (Chapter 5). This criterion may also be used to distinguish between the two possibilities. The criterion will not be applicable when $\alpha n_a = 1$. Then the distinguishability will be very limited.

If the charge transfer is established to be irreversible, using the above methods, the rate parameters may be evaluated. αn_a is the parameter that can very easily be evaluated using equations 4.2c and 4.2d. i versus log $(E - E_i)$ analysis using equation 4.52 will also provide αn_a if the i values are limited from 10 to 30 per cent of the peak current depending on v and C_{ox}. It is safer to establish that the current in this region is independent of sweep rate over a narrow range of sweep rates (say 10-40 mV/sec). n value may be obtained using equation 4.2.a if D_{ox} value is known. Preparative electrolysis at constant potential or coulometric methods may be used for this purpose if even an approximate value of D_{ox} is not accessible. However, D_{ox} values of the species or the species of similar molecular size may be available. For obtaining the remaining kinetic parameter k_h^o, we need E^o value. This is often the most difficult parameter to obtain. If E^f values could be obtained by other methods such as potentiometric titrations or spectroelectrochemical methods (Chapter 15), k_h^o may be calculated using 4.2.a. If both cathodic and anodic peaks are noticed (even with wide ΔE_p values) $E - E_i$ versus log i plots may be constructed from both the cathodic and anodic wave using equation 4.5.2. The intersection of their linear portions would then provide E^f. Rate parameters of $PtCl_4^{2-}$ redox process [44] and Cr^{3+}/Cr^{2+} redox process [45] have been evaluated by LSV method of analysis described here.

Evaluation of rate parameters in a quasi-reversible process is even an easier task using Table 4.3. The knowledge of E^f is not necessary for evaluating k_h^o of such processess. However E^f would be approximately $E_{p,a} + E_{p,c}/2$ as for reversible processes. The n value would be mostly one for such fast charge transfer processes. α value may be estimated at still higher sweep rates where irreversible charge transfer expressions may be used (Table 4.2). D_{ox} also may be evaluated again using equation 4.2.a. Now ΔE_p values at

Table 4.3

Functions for different ΔE_p values for the calculation of

$$k_h^o \cdot O_x + ne \rightleftharpoons R$$
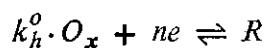
$$\psi = \frac{(D_{ox}/D_R)^{\alpha/2} \cdot k_h^o}{(D_{ox}\pi\alpha nfv)^{1/2}}$$

ΔE_p	ψ	ΔE_p	ψ
61	20	117	0.38
63	7	121	0.35
64	6	140	0.26
65	5	141	0.25
66	4	160	0.20
68	3	176	0.16
72	2	188	0.14
84	1	200	0.12
86	0.91	204	0.11
89	0.80	212	0.10
92	0.75	240	0.077
96	0.61	244	0.074
104	0.54	290	0.048
105	0.50		

Compiled from references [34] and [35]

various sweep rates may be used to evaluate k_h^o using Table 4.3 [34, 35].

The above method of evaluating k_h^o was first applied for the reduction of metal ions on Hg electrodes [34, 35] (See Chapter 6). This method was employed for estimating the k_h^o values of aromatic

hydrocarbons [46]. From then on, this method is being employed for k_h^o estimation very extensively [47, 48]. More details as well as limitations of this approach may be found in the literature [34, 35, 49].

The k_h^o values evaluated by the methods discussed above are the apparent experimental rate constants. Hence they are rightly referred to as $k_{h,app}^o$. They can be influenced by the interfacial properties. The most widely studied influence is of course the so-called double layer effect [10]. In this model, correction made for the potential difference that may exist between the point of closest approach of the reacting species towards the electrode (O.H.P. see Section 1.2) and the solution. This potential ϕ_2 is calculated using Guoy-Chapman theory of the space charge (Section 1.3) from the capacitance curves.

$$k_h^o = k_{h,ap}^o \exp \{-(\alpha n_a - Z)f\phi_2\} \qquad 4.61$$

k_h^o values may be affected even more strongly by specific adsorption, surface solvent layer, nature of the electrode material itself and the films on the electrode surface. These surface effects are not at all considered by the above double layer. We shall discuss these surface effects in greater detail later (Chapter 11).

Now, let us consider the rate constants of simple single step processes that are not influenced by any such surface effects. What are the factors that influence k_h^o? Why should there be such a vast difference in the rate of electron transfer? Which factors cause the variation of k_h^o from say 10 cm/sec [9] to 10^{-9} cm/sec [10]?

A great deal of effort has gone into the development of the theory of electron transfer from phenomenological ones [4-6] through statistical mechanical models [7-8] up to quantum mechanical theories [50-52]. The most successful among them of course are the ones based on Marcus models [7, 8]. In this model of simple electron transfer (no bond formation or bond dissociation etc.) the electron transfer rate constant may be represented by

$$k_h^o = \kappa Z \exp \left(-\frac{\Delta G^{\neq}}{RT}\right) \qquad 4.62$$

where κ is the electron tunnel transition probability (the quantum mechanical property) of electron transfer which may be considered

as unity unless an inhibiting film between the electrode surface and Ox retards the electron transfer. There is also some discussion of $k < 1$ in such simple electron transfer [53], which aspect is taken up in Chapter 11. The symbol Z in equation 4.62 refers to the frequency factor of the electron transfer which is given by $(RT/2\pi M)^{1/2}$ where M is the molecular weight of Ox [8]. This has the unit of cm/sec and represents the maximum rate attainable, when the activation free energy $\Delta G^{\neq}$ is zero. This expression for Z was discussed in detail as early as 1964 [8] but still one finds expressions for rate constants where $Z = kT/h$ which is the frequency factor for a bimolecular chemical reaction.

Since k and Z do not substantially vary with various redox species, a major component that determines the rate parameter k_h^0 of course is $\Delta G^{\neq}$. Marcus theory assumes that the activation process is mainly controlled by solvent reorganization around the Ox and R. A great deal of effort has been made to calculate this solvent reorganization energy. This idea qualitatively explains the observations very well. For example, organic compounds are generally not highly solvated and hence they are generally found to possess high k_h^0 values [9]. Inorganic aquo complexes such as Cr^{2+}/Cr^{3+} complexes show very low rate constants when compared with the complexes of other ligands [53]. H^+ is probably the strongest possible solvated ion in water and it also probably has the lowest k_h^0 value for electron transfer on H_g electrode [10]. (Bond forming catalytic reactions and bond breaking ones are not considered here). The k_h^0 value of a single redox reaction (Eu^{3+}/Eu^{2+}) is found to decrease as the complex forming capacity of the solvent increases [54]. Marcus relation is also similar to the Bronsted relation which correlates the $\Delta G^{\neq}$ with ΔG involved in the overall charge transfer process [15]. This relation is found to hold in mixed potential processes [3] and even in oxidative substitution reaction kinetics [55].

It is beyond the scope of this book to treat the theory of electron transfer itself in greater detail. The following literature would give further details in a lucid and comprehensive way [8, 9, Chapter 4 of 15, 41 and discussions in 56].

4.4.2 THE SYMMETRY FACTOR

The Marcus theory also predicts that the transfer coefficient is a

function of potential [8] in contrast with the Butler-Volmer expression [4–6] which assumes that $\alpha(\beta)$ is independent of potential. Some interesting discussions on this subject are still in progress [56]. However it is now generally agreed that α variation with potential due to solvent reorganization does take place the quantitative value being beyond experimental errors [41, 56].

It is indeed gratifying to observe that some unequivocal evidence for the variation of transfer coefficient has come from convolution sweep voltammetry [38, 57, 58]. Saveant and co-workers have used equation 4.59 to evaluate $k(E)$ at various potentials for the reduction of t-nitrobutane. The $k(E)$ values were found to show finite curvature with potential after necessary corrections for double layer effects were made. The $d \log k(E)/dE$ gave the apparent Tafel slopes $\alpha(E)$. The slope $d\alpha(E)/dE$ was found to be a constant and it agreed with the relative values of reorganization energies evaluated from k_h^0 values.

The variation of α with potential was also established by numerical simulation technique [59]. It was shown that the numerically simulated CV curves coincide very well with the experimental CV curves if α is assumed to vary according to equation 4.63.

$$\alpha = \alpha_o + \left(\frac{d\alpha}{dE}\right)(E - E^f)/2 \qquad 6.63$$

The $d\alpha/dE$ value was evaluated by the curve fitting procedure for the reduction of t-nitrobutane on Hg (Fig. 4.7) as also on Pt [59].

Interesting as they are, it is surprising that very little work has been done in this direction. There is ample scope of further research work in this line which would result in deeper understanding of charge transfer kinetics.

4.4.3 THE MULTISTEP CHARGE TRANSFERS AND TRANSFER COEFFICIENTS

In a single step process all the rate parameters are measurable quantities and hence one tries to measure each individual kinetic parameter in the process. In a multistep process, there is a sequence of events taking place (Section 4.2.2 and 4.2.3). Each step should possess 'its' own thermodynamic and kinetic parameters. However, there is still the same experimental information, simple current-potential curve as in the case of a single step process. Naturally in
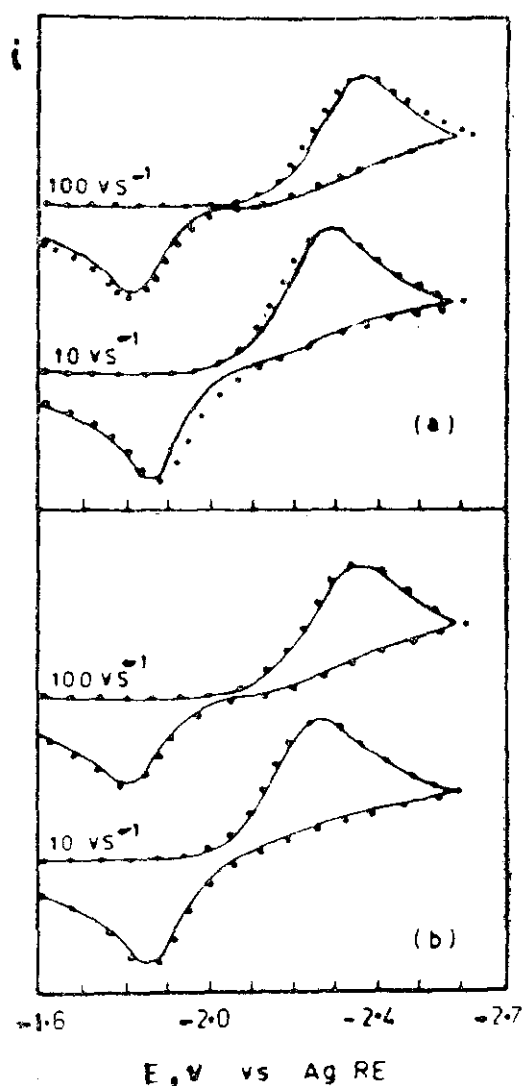
Fig. 4.7.   Cyclic voltammetric results for t-nitrobutane reduction at mercury in acetonitrile with tetra-n-butyl ammonium perchlorate electrolyte. Cathodic peak currents for 10 and 100 $V \cdot s^{-1}$ were 48 and 145 μA.

(a) Results compared with constant α simulations

(b) Results compared with potential dependent α simulations

(.....) Experimental data

(———) Simulation

[From DA Corrigan and DH Evans, J Electroanal Chem 106 (1980) 287].

such a situation, one must be satisfied with the evaluation of the sequence of processes and locating the slowest process in the sequence. This is the so-called 'reaction mechanism' analysis.

Such mechanism analysis is generally carried out by determining the Tafel slope (αn_a) and the reaction orders of each reacting species at constant potential. Tafel slopes may be easily obtained using equations 4.2c, 4.2.d, and 4.52 at the foot of the wave after ensuring the absence of mass transfer effects. Equations similar to equation 4.52 are also used for the estimation of reaction orders. For example, the current-potential expression for reaction sequence equations 4.21, 4.38 and 4.39 may be written from equation 4.44 at the foot of the wave as

$$i = nFAk_{eff}C_A^2 C_{H+} \cdot \exp\{-\beta nf(E - E_i)\} \qquad 6.64$$

From the experimentally observed αn_a values and reaction orders measured in this way, one can predict the sequence of events (Table 4.1). There is a large number of experimental works of this kind which may be referred to as example. However, one may just refer to one set of earlier works of this kind [60–62] where the derivations are explained in detail and substantiated very well with examples.

If both the reduction and oxidation waves are noticeable (with high ΔE_p values) the linear $\log i$ versus $(E - E_i)$ regions of the cathodic waves may be extended to intersect the potential axis at E_{eq}. The current at this potential is the overall exchange current density. However, the individual rate constants or equilibrium constants cannot be decoupled from this information.

4.5 APPLICATIONS AND SCOPE

In this chapter the kinetics of the central act in electrochemistry, the electron transfer, has been discussed. A great deal of work has already been done in this area using CV techniques. However, there is a lot more work that can be done in aqueous and aprotic media. Recent thermodynamic analysis [63, 64] using CV may easily be extended to kinetic work in low temperature melts. Charge transfer kinetics of biological molecules also must pick up in the near future. *In vivo* voltammetric studies (Section 3.5) are primarily oriented towards analytical applications. Kinetics of charge transfer in biological medium may be of great use in understanding biological redox processes.

LSV peak currents of irreversible and quasi-reversible charge transfer processes are directly proportional to C_{ox} at constant sweep rates. Hence they are analytical useful tools. A number of voltammetric studies reported in the literature are aimed at such analytical applications only. There is ample scope for new work in these directions. Closely related analytical techniques such as staircase voltammetry, square wave voltammetry and differential pulse voltammetry (Chapter 3) are also employed for quantitative analysis. The requirement of higher analytical sophistications, of course, leads to better sensitivities.

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