

Electrochemistry of Redox Reaction

III. On the Kinetic Equations for Chronoamperometry

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SYNOPSIS

A basic kinetic equation of potential-step chronoamperometric current-time curve controlled by the rates of diffusion and electron transfer for a simple one-electron charge transfer reaction was given and various features of current-time curves were deduced from a theoretical treatment. The current-time equations for reversible and irreversible electron transfer processes appear as special cases with limited conditions of the equation reported in the present paper. And a potential-step chronoamperometric method to determine kinetic parameters from a current-time curve was proposed therefrom. The extension of a basic kinetic equation to more general multistep charge-transfer process was also considered.

1. INTRODUCTION

In the previous papers^{1,2)}, we have dealt with the kinetic equations on the steady-state polarization voltage-current curves for a rotating disk technique and the potential-time curves for a chronopotentiometric technique from a unifying point of view.

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There have been many excellent treatments on the potential-step chronoamperometric current-time equations for various electrode processes³⁻¹⁰). However, it seems to be not adequate to apply the equations directly to the kinetic studies of redox reaction partly because the equations are only valid under the restricted conditions and partly because the direct determinations of the kinetic parameters such as the apparent exchange current density and the transfer coefficient are hardly attainable from the equations.

In this paper, we have considered a general potential-step chronoamperometric current-time relationship without any restricted conditions with respect to the kinetics of charge transfer, in which the equations for reversible and irreversible electron transfer process appear as special cases.

2. THEORY OF THE METHOD

In the case of a single elementary charge transfer reaction



which involves two soluble species, neglecting the double layer effects, the current-voltage characteristics under the potentiostatic condition may be represented by¹⁾

$$J(t) = J_0^S \cdot \left[C_R(0,t) \cdot \exp\left\{\frac{\alpha F}{RT}(E_C - E_0)\right\} - C_O(0,t) \cdot \exp\left\{-\frac{(1-\alpha)F}{RT}(E_C - E_0)\right\} \right] \quad (2)$$

where J_0^S is the apparent standard exchange current density in $\text{A} \cdot \text{cm}^{-2}$, $J(t)$ is the current density in $\text{A} \cdot \text{cm}^{-2}$ as a function of time, t is the time in seconds elapsed after the beginning of electrolysis, E_C is the controlled electrode potential with respect to reference electrode (V vs. RE) and E_0 is the standard electrode potential in V (vs. RE) for the reaction (1), while $C_R(0,t)$ and $C_O(0,t)$ are the surface concentration of the species Red and Ox, respectively, in $\text{moles} \cdot \text{cm}^{-3}$ as a function of time.

In order to derive a potential-step chronoamperometric current-time equation, the surface concentration of Red and Ox must be obtained by solving Fick's equation for linear diffusion under the following initial and boundary conditions,

$$C_O(x,t) = C_O^0, \quad C_R(x,t) = C_R^0 \quad \text{at } t = 0 \quad (3)$$

$$C_O(x,t) = C_O^0, \quad C_R(x,t) = C_R^0 \quad \text{for } x \rightarrow \infty \quad (4)$$

$$J(t) = -FD_O \left(\frac{\partial C_O(x,t)}{\partial x} \right)_{x=0} = FD_R \left(\frac{\partial C_R(x,t)}{\partial x} \right)_{x=0} \quad \text{at } t > 0 \quad (5)$$

where C_R^O and C_O^O are the concentrations of the species Red and Ox, respectively, in moles cm^{-3} in the solution of bulk.

Combination of eqs.(2) and (5) gives the boundary conditions for potential-step chronoamperometry :

$$\left(\frac{\partial C_O(x,t)}{\partial x} \right)_{x=0} = -\kappa \cdot \lambda_R \cdot C_R(0,t) + \lambda_O \cdot C_O(0,t) \quad (6)$$

$$\left(\frac{\partial C_R(x,t)}{\partial x} \right)_{x=0} = \lambda_R \cdot C_R(0,t) - \frac{\lambda_O}{\kappa} C_O(0,t) \quad (7)$$

at $t > 0$, with

$$\lambda_O = \frac{J_O^S}{FD_O} \exp\left\{-\frac{(1-\alpha)F}{RT} (E_C - E_O)\right\} \quad (8)$$

$$\lambda_R = \frac{J_O^S}{FD_R} \exp\left\{\frac{\alpha F}{RT} (E_C - E_O)\right\} \quad (9)$$

$$\kappa = \frac{D_R}{D_O} \quad (10)$$

By taking the Laplace transforms of the Fick's equation and the boundary conditions ((4), (6), and (7)) and solving the second-order ordinary differential equations under the given initial and boundary conditions, and then returning to the functions $C_R(x,t)$ and $C_O(x,t)$ and substituting them into eq.(2) with $x = 0$, finally one has

$$\frac{J(t)}{J_O^S} = \left[C_R^O \cdot \exp\left\{\frac{\alpha F}{RT} (E_C - E_O)\right\} - C_O^O \cdot \exp\left\{-\frac{(1-\alpha)F}{RT} (E_C - E_O)\right\} \right] \cdot \exp(\lambda^2 t) \operatorname{erfc}(\lambda \sqrt{t}) \quad (11)$$

with

$$\begin{aligned} \lambda &= \lambda_O \sqrt{D_O} + \lambda_R \sqrt{D_R} \\ &= \frac{J_O^S}{F} \cdot \left[\frac{1}{\sqrt{D_R}} \exp\left\{\frac{\alpha F}{RT} (E_C - E_O)\right\} + \frac{1}{\sqrt{D_O}} \exp\left\{-\frac{(1-\alpha)F}{RT} (E_C - E_O)\right\} \right] \quad (12) \end{aligned}$$

3. NATURE OF THE FUNCTION $\exp(\lambda^2 t) \cdot \operatorname{erfc}(\lambda\sqrt{t})$

Since the shape of current-time curve was indicated to be simply determined by the function $\exp(\lambda^2 t) \cdot \operatorname{erfc}(\lambda\sqrt{t})$ because the bracket in eq.(11) was constant under a given condition, it is necessary to understand the nature of the function.

Approximation of the function can be done for large and for small value of $\lambda\sqrt{t}$ ¹¹⁾. For small value of $\lambda\sqrt{t}$, $\operatorname{erf}(\lambda\sqrt{t})$ can be expanded to the following series ;

$$\operatorname{erf}(\lambda\sqrt{t}) = \frac{2}{\sqrt{\pi}} \left\{ \lambda\sqrt{t} + \sum_{n=1}^{\infty} \frac{(-1)^n (\lambda\sqrt{t})^{2n+1}}{(2n+1)n!} \right\} \quad (13)$$

and consequently

$$\exp(\lambda^2 t) \cdot \operatorname{erfc}(\lambda\sqrt{t}) = \exp(\lambda^2 t) \cdot \left[1 - \operatorname{erf}(\lambda\sqrt{t}) \right] \quad (14)$$

can be obtained.

Conversely, for large value of $\lambda\sqrt{t}$, $\exp(\lambda^2 t) \cdot \operatorname{erfc}(\lambda\sqrt{t})$ can be represented as

$$\begin{aligned} & \exp(\lambda^2 t) \cdot \operatorname{erfc}(\lambda\sqrt{t}) \\ &= \frac{1}{\sqrt{\pi}} \left\{ \frac{1}{\lambda\sqrt{t}} - \frac{1}{2(\lambda\sqrt{t})^3} + \dots + (-1)^{n-1} \frac{1 \cdot 3 \cdot \dots \cdot (2n-3)}{2^{n-1} \cdot (\lambda\sqrt{t})^{2n-1}} \right\} \quad (15) \end{aligned}$$

Since the series in eq.(15) does not converge, one should take finite terms of the series.

Figure 1 shows the nature of the function $\exp(\lambda^2 t) \cdot \operatorname{erfc}(\lambda\sqrt{t})$. Curve (a) is obtained by calculating the sum of the terms up to 11th term in eq.(13) combined with eq.(14). Curves (b) and (c) are obtained by calculating the sum of the terms up to 5th and 4th term, respectively, in eq.(15) as an approximation. The solid line in Fig.1 indicates the values calculated from eq.(14) with the results of the computer-assisted numerical integration on $\operatorname{erf}(\lambda\sqrt{t})$, which was confirmed by the numerical table¹²⁾.

According to Fig.1, if one takes the 11-terms sum in eq.(13) combined with eq.(14) as an approximation for the function, it gives precise values of the function for 0 to 1.5 in $\lambda\sqrt{t}$, and if one takes the 4-terms or 5-terms sum in eq.(15), the approximation is fairly good for the values of $\lambda\sqrt{t}$ greater than 2.

Further approximation can be done under the more restricted conditions. For the value of $\lambda\sqrt{t}$ less than 0.02, the terms in eq.(13) except the first term can be dropped and consequently one can take

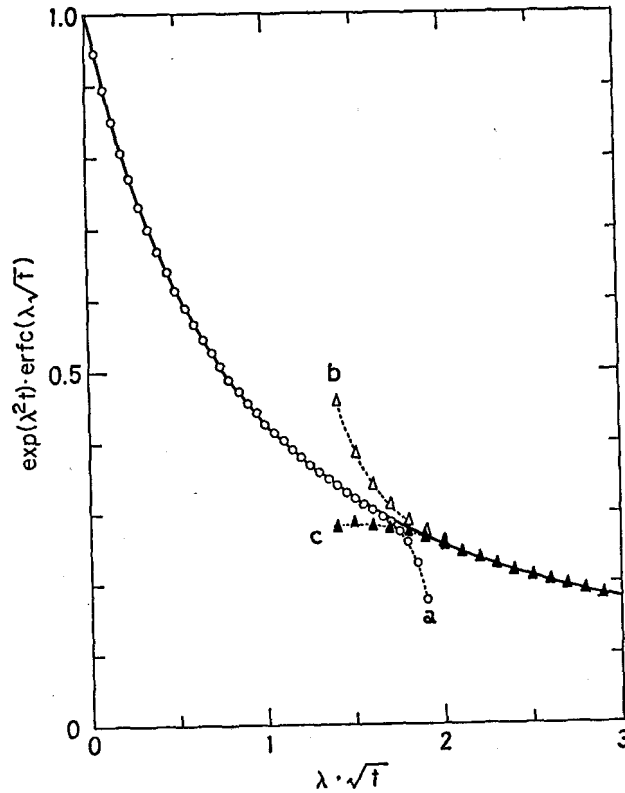


Fig.1 The nature of the function $\exp(\lambda^2 t) \cdot \text{erfc}(\lambda\sqrt{t})$
 Solid line : from eq.(14) combined with the results of the numerical integration on $\text{erf}(\lambda\sqrt{t})$
 Dashed line (a) : from the sum up to 11th term in eq.(13)
 Dashed line (b) : from the sum up to 5th term in eq.(15)
 Dashed line (c) : from the sum up to 4th term in eq.(15)

$$\exp(\lambda^2 t) \cdot \text{erfc}(\lambda\sqrt{t}) = 1 - \frac{2\lambda\sqrt{t}}{\sqrt{\pi}} \quad \text{for } \lambda\sqrt{t} < 0.02 \quad (16)$$

as an approximation for the function.

On the other hand, the second term to n th term in eq.(15) can be dropped for the value of $\lambda\sqrt{t}$ greater than 4 and then one can take

$$\exp(\lambda^2 t) \cdot \text{erfc}(\lambda\sqrt{t}) = \frac{1}{\lambda\sqrt{\pi t}} \quad \text{for } \lambda\sqrt{t} > 4 \quad (17)$$

as an approximation.

4. POTENTIAL-STEP CHRONOAMPEROMETRIC CURRENT-TIME CHARACTERISTICS

Since the function $\exp(\lambda^2 t) \cdot \operatorname{erfc}(\lambda\sqrt{t})$ was known, one can figure out the potential-step chronoamperometric current-time characteristics from eq.(11).

Before electrolysis, the bracket in eq.(11) should be zero and consequently the electrode potential E_e before electrolysis can be calculated to be

$$E_e = E_O - \frac{RT}{F} \ln \frac{C_R^O}{C_O^O} \quad (18)$$

Equation (18) is the another expression of the condition (3).

When the step function signal of voltage E_C is imposed on the system at $t = 0$, the current will begin to flow with the relationship of eq.(11).

By introducing eq.(16) for the value of $\lambda\sqrt{t}$ less than 0.02, one obtains

$$\frac{J(t)}{J_O^S} = \left[C_R^O \cdot \exp\left\{\frac{\alpha F}{RT}(E_C - E_O)\right\} - C_O^O \cdot \exp\left\{-\frac{(1-\alpha)F}{RT}(E_C - E_O)\right\} \right] \cdot \left[1 - \frac{2\lambda\sqrt{t}}{\sqrt{\pi}} \right] \quad (19)$$

$$\text{for } t < \frac{0.0004}{\lambda^2} \quad (20)$$

where λ is given by eq.(12).

In eq.(19), when one of the terms in the bracket is much greater than the other, one of the terms can be dropped and then eq.(19) becomes

$$J(t) = C_R^O \cdot J_O^S \cdot \exp\left\{\frac{\alpha F}{RT}(E_C - E_O)\right\} \cdot \left[1 - \frac{2\lambda\sqrt{t}}{\sqrt{\pi}} \right] \quad (21)$$

$$\text{for } E_C \gg E_O - \frac{RT}{F} \ln \frac{C_R^O}{C_O^O} \quad (22)$$

$$\text{or } J(t) = -C_O^O \cdot J_O^S \cdot \exp\left\{-\frac{(1-\alpha)F}{RT}(E_C - E_O)\right\} \cdot \left[1 - \frac{2\lambda\sqrt{t}}{\sqrt{\pi}} \right] \quad (23)$$

$$\text{for } E_C \ll E_O - \frac{RT}{F} \ln \frac{C_R^O}{C_O^O} \quad (24)$$

The right hand sides of the equations (22) and (24) correspond to the electrode potential E_e before electrolysis as was given in eq.(18).

Equations (19), (21), and (23), which are formally the same as described by Delahay^{5,6}, Gerischer and Vielstich⁷, indicate that the straight lines can be observed in the $J(t)$ vs. \sqrt{t} plots under the condition $t < 0.0004/\lambda^2$ and consequently one can easily determine the kinetic parameters J_O^S and α .

For an another extreme case, by introducing eq.(17) for the value of $\lambda\sqrt{t}$ greater than 4, one obtains

$$J(t) = \left[\frac{C_R^O \cdot \exp\left\{\frac{\alpha F}{RT}(E_C - E_O)\right\} - C_O^O \cdot \exp\left\{-\frac{(1-\alpha)F}{RT}(E_C - E_O)\right\}}{\frac{1}{\sqrt{D_R}} \exp\left\{\frac{\alpha F}{RT}(E_C - E_O)\right\} + \frac{1}{\sqrt{D_O}} \exp\left\{-\frac{(1-\alpha)F}{RT}(E_C - E_O)\right\}} \right] \cdot \frac{F}{\sqrt{\pi t}} \quad (25)$$

$$\text{for } t > \frac{16}{\lambda^2} \quad (26)$$

In eq.(25), when $|E_C - E_O| \gg RT/\alpha F$, $RT/(1-\alpha)F$, the equation reduces to the following simple expressions ;

$$J(t) = \frac{F \cdot C_R^O \cdot \sqrt{D_R}}{\sqrt{\pi}} \cdot \frac{1}{\sqrt{t}} \quad (27)$$

or

$$J(t) = \frac{-F \cdot C_O^O \cdot \sqrt{D_O}}{\sqrt{\pi}} \cdot \frac{1}{\sqrt{t}} \quad (28)$$

These equations are sometimes referred as the Cottrell equation³).

Equations (25), (27), and (28) mean that the $J(t)$ vs. $1/\sqrt{t}$ plots give a straight line for $t > 16/\lambda^2$ and the diffusion coefficient D_O and/or D_R can be obtained therefrom.

Although equations (19), (25) and their derivatives are important relationships on chronoamperometry, they only cover the part of the current-time curves, that is, major part of the current-decay curves, $0.0004/\lambda^2 < t < 16/\lambda^2$, still remains void.

Although it is possible to figure out current transient by using eq.(11) for any J_O^S , C_R^O , C_O^O , α , E_C , E_O , D_R , and D_O , it is convenient to consider the following case.

Putting $C_O^O = C_R^O = C$, $D_R = D_O = D$, and $E_C - E_O = \eta$, equations (11) and (12) become

$$\frac{J(t)}{J_O^S \cdot C} = \left[\exp\left(\frac{\alpha F}{RT} \cdot \eta\right) - \exp\left(-\frac{(1-\alpha)F}{RT} \cdot \eta\right) \right] \exp(\lambda^2 t) \cdot \text{erfc}(\lambda\sqrt{t}) \quad (29)$$

with

$$\lambda = \frac{J_O^S}{F\sqrt{D}} \cdot \left[\exp\left(\frac{\alpha F}{RT} \cdot \eta\right) + \exp\left(-\frac{(1-\alpha)F}{RT} \cdot \eta\right) \right] \quad (30)$$

The conditions $C_O^0 = C_R^0$ and $D_O = D_R$ are not serious limitations because $C_O^0 = C_R^0$ can be fulfilled under an experimental condition and because the values of $D_R = D_O$ are the same order of magnitude in an ordinary solution.

Since $\exp(\lambda^2 t) \cdot \text{erfc}(\lambda\sqrt{t})$ is unity at $t = +0$ in eq.(29), the current at $t = +0$ corresponds to that of no mass transport effect.

The effect of transfer coefficient on the current-applied voltage characteristics at $t = +0$ was shown in Fig.2. Figure 2 indicates that one can easily determine J_O^S and α if the current at $t = +0$ can be obtained.

The effects of the apparent standard exchange current density J_O^S and applied voltage-step η on current transient were shown in Figs.3 and 4.

On the same time scale, J_O^S and η affect the shape of the current-time curves as were illustrated in Figs.3 and 4. It should be noted that the shape of the current-time curve is the same with respect to

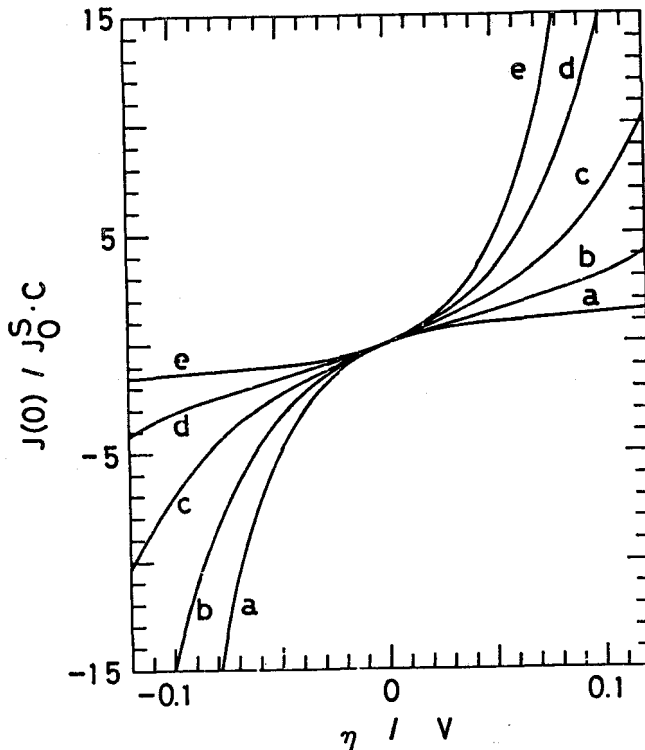


Fig.2 The effect of transfer coefficient on the shape of the zero-time current-overvoltage curves. $T = 298 \text{ }^\circ\text{K}$

α : (a) 0.1, (b) 0.3, (c) 0.5, (d) 0.7, and (e) 0.9

the time factor $\lambda\sqrt{t}$ as was indicated in eq.(11) and that the current transient with respect to real time t highly depend on the values of J_O^S , E_C , D_O , and D_R .

5. SIGNIFICANCE OF THE EQUATION ON DETERMINING KINETIC PARAMETERS

Since the shape of the current-time curve is simply determined by the function $\exp(\lambda^2 t) \cdot \text{erfc}(\lambda\sqrt{t})$ and the absolute value of the current is controlled by the factor

$$J_O^S \cdot \left[C_R^O \cdot \exp\left\{\frac{\alpha F}{RT}(E_C - E_O)\right\} - C_O^O \cdot \exp\left\{-\frac{(1-\alpha)F}{RT}(E_C - E_O)\right\} \right]$$

according to the analytical results of eq.(11), the following rapid estimation of J_O^S and more precise determinations of the kinetic

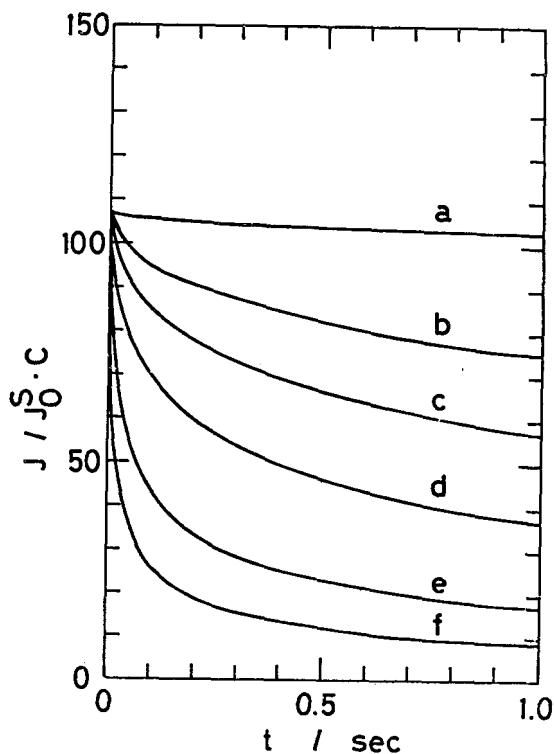


Fig.3 The effect of the apparent standard exchange current density on the shape of current-time curves

$\eta = 0.24$ V, $\alpha = 0.5$, $T = 298$ °K, $D = 1 \times 10^{-5}$ cm²·sec⁻¹.

J_O^S : (a) 0.1, (b) 1, (c) 2, (d) 4, (e) 10 and (f) 20 A·cm⁻².

parameters would be possible.

As was indicated by eq.(11), real time current response only depends on the value of λ which is independent of the concentration of C_O^0 and C_R^0 , i.e., rapid decrease in current means large value of λ and conversely slow decrease means small value of λ as were illustrated in Fig.3 and 4.

According to eq.(12), the value of λ is mainly influenced by J_0^S under a given experimental condition. Consequently, if one has well-defined current-time curves, one can determine D_R and D_O from eqs.(27) and (28) and also determine J_0^S and α by using a curve-fitting method based on eqs.(11) and (12) after estimating J_0^S and α from eq.(19) and its relatives.

In the present study, the double-layer charging effects was not

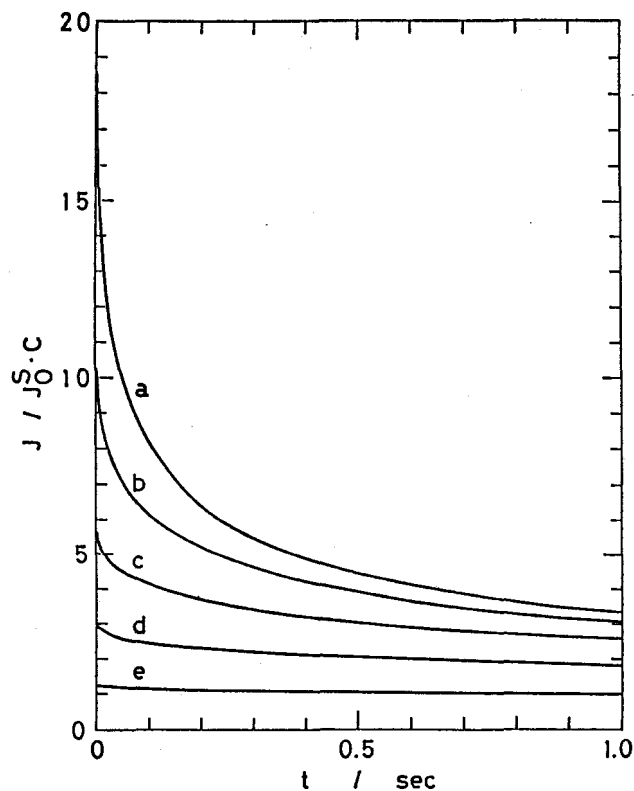


Fig.4 The effect of applied voltage-step on the shape of current-time curves.

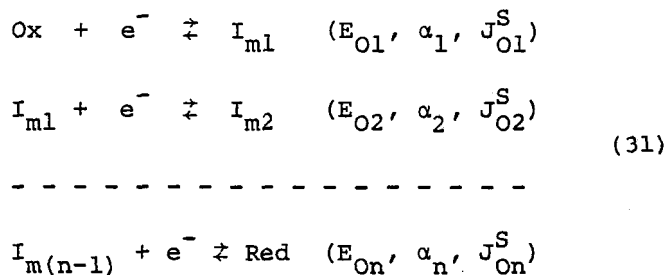
$$\alpha = 0.5, T = 298 \text{ } ^\circ\text{K}, J_0^S = 50 \text{ A}\cdot\text{cm}^{-2}, D = 1 \times 10^{-5} \text{ cm}^2\cdot\text{sec}^{-1}.$$

η : (a) 0.15, (b) 0.12, (c) 0.09, (d) 0.06 and (e) 0.03 V.

considered. If the effects existed in an electrode system, one should have an initial spike in the current-time curve. The large value of J_0^S , however, also gives an initial spike in the curve even without any double-layer charging effect as was demonstrated in Fig.3. The difference between them is the value of the current at $t = + 0$, that is, one is an infinite current and the other is a finite current as was illustrated in Fig.1. Further considerations is out of purpose in this paper, which will appear in a separate paper describing experimental results together with the network analysis of the system including an experimental cell and a potentiostat.

6. EXTENSION OF THE EQUATION TO MULTISTEP CHARGE TRANSFER REACTION

For a hypothetical n-step reaction with consecutive n-electrons transfer^{1,2)}



by solving the Fick's equations under the corresponding initial and boundary conditions to eqs.(3), (4), (6), and (7), the potential-step chronoamperometric current-time characteristics may be represented as

$$J(E) = n \cdot (AC_R^O - BC_O^O) \exp(\xi^2 t) \text{erfc}(\xi \sqrt{t}) \tag{32}$$

with
$$\xi = \frac{A}{F\sqrt{D_R}} + \frac{B}{F\sqrt{D_O}} \tag{33}$$

where
$$A = \frac{\exp\{\sum_{i=1}^n \alpha_i \cdot G_i + \sum_{i=2}^n (1 - \alpha_i) G_i\}}{\frac{1}{J_{O1}^S} + \sum_{k=2}^n \frac{1}{J_{Ok}^S} \exp\{\sum_{i=1}^{k-1} \alpha_i \cdot G_i + \sum_{i=2}^k (1 - \alpha_i) G_i\}} \tag{34}$$

and
$$B = \frac{\exp\{-(1 - \alpha_1) G_1\}}{\frac{1}{J_{O1}^S} + \sum_{k=2}^n \frac{1}{J_{Ok}^S} \exp\{\sum_{i=1}^{k-1} \alpha_i \cdot G_i + \sum_{i=2}^k (1 - \alpha_i) G_i\}} \tag{35}$$

with

$$G_i = \frac{F(E_C - E_{O_i})}{RT} \quad (36)$$

where E_C is the controlled electrode potential, $J(t)$ is the current density as a function of time, while α_i , E_{O_i} , and $J_{O_i}^S$ are the transfer coefficient, the standard electrode potential and the apparent standard exchange current density, respectively, for the elementary step i . It was assumed that Ox and Red were the diffusing species and the intermediate did not diffuse away from an electrode surface.

Before electrolysis, i.e., $J(t) = 0$ at $t \leq 0$, equation (32) becomes

$$E = E_O - \frac{RT}{nF} \ln \frac{C_R^O}{C_O} \quad (37)$$

with

$$E_O = \frac{1}{n} \cdot \sum_{i=1}^n E_{O_i}$$

Equation (37) represents the equilibrium potential before electrolysis for the reaction $Ox + ne^- \rightleftharpoons Red$.

When $J_{O_i, i \neq m}^S \gg J_{O_m}^S$ which corresponds to the consecutive electrochemical reaction with single rate-determining step, the current-time curves for oxidation and reduction processes may be given by

$$J(t) = n \cdot C_R^O \cdot J_{O_m}^S \cdot \exp\left\{ \sum_{i=m}^n G_i - (1 - \alpha_m) G_m \right\} \cdot \exp(\xi^2 t) \operatorname{erfc}(\xi \sqrt{t}) \quad (38)$$

for

$$E_C \gg E_O - \frac{RT}{nF} \ln \frac{C_R^O}{C_O},$$

or

$$J(t) = -n \cdot C_O^O \cdot J_{O_m}^S \cdot \exp\left\{ \alpha_m \cdot G_m - \sum_{i=1}^m G_i \right\} \cdot \exp(\xi^2 t) \operatorname{erfc}(\xi \sqrt{t}) \quad (39)$$

for

$$E_C \ll E_O - \frac{RT}{nF} \ln \frac{C_R^O}{C_O}$$

with

$$\xi = \frac{J_{O_m}^S}{F} \cdot \left[\frac{\exp\left\{ \sum_{i=m}^n G_i - (1 - \alpha_m) G_m \right\}}{\sqrt{D_R}} + \frac{\exp\left\{ \alpha_m \cdot G_m - \sum_{i=1}^m G_i \right\}}{\sqrt{D_O}} \right] \quad (40)$$

Accordingly, equation (32) with eqs.(33) to (36) may be more general expression than eq.(11) for the potential-step chronoamperometric current-time curves.

CONCLUDING REMARKS :

In order to bridge the gap between theoretical electrochemistry and electrochemical engineering, we have dealt with the basic kinetic equations for the electrochemical reactions of soluble redox species and partly succeeded to bridge the gap between them to give the kinetic equations on determining kinetic parameters, i.e., rotating disk technique, chronopotentiometric technique and chronoamperometric technique.

The basic concept of the series of treatments is the consideration on a unifying kinetic equation without assuming any rate-determining step from which the kinetic equations assuming a rate-determining step appear as special cases. Therefore, the basic kinetic equations in this paper and the previous papers may be applicable to the prediction on the characteristics of electrochemical redox reaction.

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APPENDIX : Derivation of equation (11)

By taking the Laplace transforms of the Fick's equations on $C_R(x,t)$ and $C_O(x,t)$ and solving the second-order ordinary differential equations under the initial condition (3) and the boundary condition (4), whose solutions are

$$C_O(x,s) = B_1 \exp\left(-\sqrt{\frac{s}{D_O}} \cdot x\right) + \frac{C_O^0}{s} \quad (\text{A-1})$$

$$C_R(x,s) = B_2 \exp\left(-\sqrt{\frac{s}{D_R}} \cdot x\right) + \frac{C_R^0}{s} \quad (\text{A-2})$$

where $C_{O,R}(x,s)$ is the transform of the function $C_{O,R}(x,t)$, B_1 and B_2 are the constants to be determined, and s is the parameter resulting from the transformation.

Since variables in the right-hand side of eq.(2) are independent of each other, λ_O and λ_R defined by eqs.(8) and (9) are independent of time t , consequently one can take the Laplace transforms of eqs.(6) and (7) without any ambiguity due to the dependent variables.

Differentiating eqs.(A-1) and (A-2) with respect to x and putting $x = 0$, and then substituting them into the transforms of eqs.(6) and (7), and finally by solving the two linear equations, the constants B_1 and B_2 can be obtained ;

$$B_1 = \frac{A}{s(\lambda + \sqrt{s})} \quad (\text{A-3})$$

$$B_2 = -\frac{A/\sqrt{k}}{s(\lambda + \sqrt{s})} \quad (\text{A-4})$$

with

$$A = (\kappa \cdot \lambda_R \cdot C_R^0 - \lambda_O \cdot C_O^0) \cdot \sqrt{D_O} \quad (\text{A-5})$$

$$\lambda = \lambda_O \cdot \sqrt{D_O} + \lambda_R \cdot \sqrt{D_R} \quad (\text{A-6})$$

By taking the inverse transforms of eqs.(A-1) and (A-2) with B_1 and B_2 given by eqs.(A-3) and (A-4), one obtains

$$C_O(x,t) = C_O^0 + \frac{A}{\lambda} \left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{D_O t}}\right) - \exp\left(\frac{\lambda}{\sqrt{D_O}} \cdot x + \lambda^2 t\right) \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{D_O t}} + \lambda\sqrt{t}\right) \right\} \quad (\text{A-7})$$

$$C_R(x,t) = C_R^0 - \frac{A}{\sqrt{k} \cdot \lambda} \left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{D_R t}}\right) - \exp\left(\frac{\lambda}{\sqrt{D_R}} \cdot x + \lambda^2 t\right) \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{D_R t}} + \lambda\sqrt{t}\right) \right\} \quad (\text{A-8})$$

Putting $x = 0$ in eqs.(A-7) and (A-8), and then putting them into eq.(2), one finally obtains eq.(11).

Thus obtained final solution eq.(11) does not have any ambiguity due to the dependent variables during the mathematical operations.

LIST OF SYMBOLS

$J(t)$	Current density as a function of time ($A \cdot cm^{-2}$)
J_O^S	Apparent standard exchange current density based on 1 mole $\cdot cm^{-3}$ as a standard ($A \cdot cm^{-2}$)
$J_{O_i}^S$	Apparent standard exchange current density for i th step charge transfer reaction ($A \cdot cm^{-2}$)
E_C	Controlled electrode potential with respect to reference electrode (V)
E_O	Standard electrode potential with respect to reference electrode in equation for electrode reaction (V)
E_{O_i}	Standard electrode potential with respect to reference electrode for i th step electrode reaction (V)
α	Transfer coefficient (-)
α_i	Transfer coefficient for i th step charge transfer reaction (-)
$C_i(x,t)$	Concentration of species i at location x as a function of time (moles $\cdot cm^{-3}$)
C_i^O	Concentration of species i in the solution of bulk (moles $\cdot cm^{-3}$)
D_i	Diffusion coefficient of diffusing species i ($cm^2 \cdot sec^{-1}$)
t	Time (sec)
x	Distance from electrode surface (cm)
s	Parameter resulting from the Laplace transformation (-)
T	Temperature ($^{\circ}K$)
F	Faraday's constant (coul $\cdot equiv^{-1}$)
R	Gas constant (joul $\cdot mole^{-1} \cdot deg^{-1}$)