A Contribution to the Theory of Pulse Polarography. I. Theory of Current-Potential Curves

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A general theory of pulse polarographic current-potential curves is developed for a simple electrode reaction proceeding at the expanding plane electrode. It is shown that when the ratio of the sampling time to the pre-electrolysis time is smaller than 1/30, this condition being satisfied in usual pulse polarographic practice, the equation of current-potential curves can be greatly simplified. The theory developed is applied to the three modes of pulse polarography nowadays practically employed, *i.e.*, normal pulse, scan-reversal pulse and differential pulse polarography. For each mode, the dependence of current-potential curves on the kinetic parameters of electrode reaction as well as on the experimental variables is discussed.

Pulse polarography, originally devised by Barker[1] as an outcome of his work on square wave polarography, has become one of the most powerful and widely used electroanalytical techniques. Nowadays, this technique is successfully employed in routine works for chemical analysis of both inorganic and organic compounds, especially for trace analysis because of its high sensitivity.

A great potentiality of pulse polarography has been recognized also for the characterization of the mechanism of electrode reactions. Thus, the theoretical studies have been made extensively by Los and coworkers[2] and Galvez and Serna[3] for various types of limiting currents, *i.e.*, the diffusion-controlled, kinetic and catalytic currents. However, the theory of current-potential curves has not yet made significant progress and so pulse polarography seems not to realize sufficiently its great potentiality for the study of electrode kinetics. Oldham[4] reported a general theory of the potential pulse electrolysis for the stationary plane electrode and thus his results can not be applied quantitatively to the pulse polarographic conditions using the dropping mercury electrode (DME). Recently, Ruzic[5] has developed a general theory of pulse polarography, but the explicit equations derived by him hold only for the case, in which the pulse duration is short enough so that the d.c. component does not change appreciably during the pulse application. Birke[6] also published a theory of differential pulse polarography, in which he made, however, some simplifying assumption which were not well justified.

In view of the great potentiality of pulse polarography in studies of electrode kinetics, it is desirable to complete the theory of pulse polarographic waves, *i.e.*, to derive the explicit general equation of current-potential curves. In the present paper, we shall attempt such an approach and present explicit equations for several modes of pulse polarography nowadays practically used.

General Equation of Current-Potential Curves

Consider a simple electrode reaction, designated by

$$\mathrm{Ox} + ne \rightleftarrows \mathrm{Red} \tag{1}$$

where both reactants Ox and Red are assumed to be soluble in solution or in DME. It is also assumed that (a) the electrode reaction (1) proceeds at the expanding plane electrode, which has been recognized as a good mathematical model of DME, and (b) the bulk of the solution contains only the reactant Ox. Then, the concentrations of Ox and Red at the electrode surface, C_O^s and C_R^s, can be expressed by[7]

$$C_O^s = C_O^\circ - \sqrt{\frac{7}{3\pi}}\frac{1}{\sqrt{D_O}}\int_0^t \frac{(i/nFq)u^{2/3}}{\sqrt{t^{7/3}-u^{7/3}}}\mathrm{d}u \tag{2}$$

$$C_R^s = \sqrt{\frac{7}{3\pi}}\frac{1}{\sqrt{D_R}}\int_0^t \frac{(i/nFq)u^{2/3}}{\sqrt{t^{7/3}-u^{7/3}}}\mathrm{d}u \tag{3}$$

where C_O° is the bulk concentration of Ox, D_O, and D_R denote the diffusion coefficients of Ox and Red, respectively, t is the time elapsed after the drop growth has begun, i the instantaneous faradaic current and q the surface area of DME. The faradaic current density is expressed as a function of the electrode potential and of the concentrations of Ox and Red at the electrode surface. According to the usual kinetic theory of electrode processes,[8] we have

$$i = nFq\{\vec{k}C_O^s - \overleftarrow{k}C_R^s\} \tag{4}$$

with

$$\begin{aligned}\vec{k} &= k_0 \exp[-(\alpha nF/RT)(E-E^\circ)]\\ \overleftarrow{k} &= k_0 \exp[\{(1-\alpha)nF/RT\}(E-E^\circ)]\end{aligned} \tag{5}$$

where E is the electrode potential, E° the formal standard potential of the reaction (1), α the cathodic transfer coefficient, k_0 the standard rate constant and F, R and T have their usual significance. Introducing Eqs. 2 and 3 into Eq. 4 yields

$$(i/nFq) = \vec{k}C_O^\circ - \sqrt{\frac{7}{3\pi}}\lambda\int_0^t \frac{(i/nFq)u^{2/3}}{\sqrt{t^{7/3}-u^{7/3}}}\mathrm{d}u \tag{6}$$

with

$$\begin{aligned}\lambda &= (\vec{k}/\sqrt{D_O}) + (\overleftarrow{k}/\sqrt{D_R})\\ &= (k_0/\sqrt{D})[\exp(-\alpha\zeta) + \exp\{(1-\alpha)\zeta\}]\end{aligned} \tag{7}$$

$$\zeta = (nF/RT)(E-E_{1/2}^r) \tag{8}$$

$$E_{1/2}^r = E^\circ - (RT/nF)\ln\sqrt{D_O/D_R} \tag{9}$$

$$D = D_O^{1-\alpha}D_R^{\alpha} \tag{10}$$

where $E_{1/2}^r$ denotes the polarographic reversible half-wave potential. Equation 6 is the Volterra integral equation of second kind with respect to (i/nFq), whose solution gives the general expression for the current-potential-time relationship of the potential-controlled electrolysis.

In the pulse polarographic conditions, the potential of DME is set on a constant value E_1 from the beginning of the drop growth to some time τ, and at $t=\tau$ it is stepped up from E_1 to the other constant value E_2. Therefore, if we write the current intensities during the periods $0<t<\tau$ and $\tau<t$ as i_1 and i_2, respectively, the electrolysis condition can be expressed as

$$0<t<\tau:\ E=E_1,\ i=i_1(t) \tag{11a}$$

$$\tau<t\quad:\ E=E_2,\ i=i_2(t) \tag{11b}$$

First, consider the electrolysis during the period $0<t<\tau$. Introducing Eq. 11a into Eqs. 6—8 yields

$$(i_1/nFq) = \vec{k}_1C_\mathrm{O}^\circ - \sqrt{\frac{7}{3\pi}}\lambda_1\int_0^t\frac{(i_1/nFq)u^{2/3}}{\sqrt{t^{7/3}-u^{7/3}}}\mathrm{d}u \tag{12}$$

with

$$\begin{aligned}\lambda_1 &= (\vec{k}_1/\sqrt{D_\mathrm{O}})+(\overleftarrow{k}_1/\sqrt{D_\mathrm{R}})\\ &= (k_0/\sqrt{D})[\exp(-\alpha\zeta_1)+\exp\{(1-\alpha)\zeta_1\}]\end{aligned} \tag{13}$$

$$\zeta_1 = (nF/RT)(E_1-E_{1/2}^\mathrm{r}) \tag{14}$$

The solution of the Volterra integral Eq. 12 was already obtained in a previous paper.[9] We have

$$i_1 = \frac{(i_\mathrm{d}^\mathrm{c})_\mathrm{Ilk}}{1+\exp(\zeta_1)}\sqrt{3\pi/7}(\lambda_1\sqrt{t})\psi(\lambda_1\sqrt{t}) \tag{15}$$

where

$$\psi(\lambda_1\sqrt{t}) = \sum_{\nu=0}^{\infty}(-1)^\nu a_\nu(\sqrt{3/7}\ \lambda_1\sqrt{t})^\nu \tag{16a}$$

with

$$a_0=1,\ a_\nu=\prod_{\mu=1}^{\nu}\left\{\Gamma\left(\frac{3\mu+7}{14}\right)\Big/\Gamma\left(\frac{3\mu+14}{14}\right)\right\} \tag{16b}$$

and

$$(i_\mathrm{d}^\mathrm{c})_\mathrm{Ilk} = \sqrt{7/3}\,nFq\sqrt{D_\mathrm{O}}C_\mathrm{O}^\circ/\sqrt{\pi t} \tag{17}$$

In the above equations, Γ denotes Euler's Gamma function and $(i_\mathrm{d}^\mathrm{c})_\mathrm{Ilk}$ the instantaneous diffusion current of d.c. polarography given by the Ilkovic equation. For numerical calculations of the function $\psi(\lambda_1\sqrt{t})$, it is convenient to use the following approximate equation derived previously,[10] which holds in the whole range of the argument within an error of 0.2%:

$$\psi(\lambda_1\sqrt{t}) = \sqrt{\frac{7}{3\pi}}\frac{g(\lambda_1\sqrt{t})/(\lambda_1\sqrt{t})}{1+g(\lambda_1\sqrt{t})} \tag{18}$$

with

$$\begin{aligned}g(\lambda_1\sqrt{t}) &= 0.293(\lambda_1\sqrt{t})\\ &\times[\tanh\{1.3\log(\lambda_1\sqrt{t}/1.61)\}+4.96]\end{aligned} \tag{19}$$

Next, we shall obtain the solution of the Volterra integral Eq. 6 for the period $t>\tau$. We write, thereafter, $\tau+\theta$ instead of t. Then, introducing Eqs. 11a and 11b into Eq. 6, we have

$$(i_2/nFq) = \vec{k}_2C_\mathrm{O}^\circ-\sqrt{7/3\pi}\ \lambda_2(I_1+I_2) \tag{20}$$

with

$$I_1 = \int_0^\tau\frac{(i_1/nFq)u^{2/3}}{\sqrt{(\tau+\theta)^{7/3}-u^{7/3}}}\mathrm{d}u \tag{21}$$

$$I_2 = \int_\tau^{\tau+\theta}\frac{(i_2/nFq)u^{2/3}}{\sqrt{(\tau+\theta)^{7/3}-u^{7/3}}}\mathrm{d}u \tag{22}$$

where

$$\begin{aligned}\lambda_2 &= (\vec{k}_2/\sqrt{D_\mathrm{O}})+(\overleftarrow{k}_2/\sqrt{D_\mathrm{R}})\\ &= (k_0/\sqrt{D})[\exp(-\alpha\zeta_2)+\exp\{(1-\alpha)\zeta_2\}]\end{aligned} \tag{23}$$

$$\zeta_2 = (nF/RT)(E_2-E_{1/2}^\mathrm{r}) \tag{24}$$

In appendix, the integrals I_1 and I_2 will be evaluated as a power series of $\sqrt{\theta/\tau}$ under the assumption that $\theta/\tau<1$. Thus, introducing Eqs. A-8 and A-9 into Eq. 20, we obtain, after some rearrangements,

$$\begin{aligned}(i_2/nFq) &= \sqrt{D_\mathrm{O}}C_\mathrm{O}^\circ\left[\frac{1}{1+\exp(\zeta_2)}-\frac{1}{1+\exp(\zeta_1)}\right]\lambda_2\\ &+\left[\frac{i_1(\tau)}{nFq(\tau)}\right]\left[\frac{\lambda_2}{\lambda_1}\right]\left\{1+\left[\frac{\mathrm{d}\ln\psi}{\mathrm{d}\ln\tau}\right]\left[\frac{\theta}{\tau}\right]+O([\theta/\tau]^2)\right\}\\ &+\left[\frac{i_1(\tau)}{nFq(\tau)}\right]\frac{2}{\sqrt{\pi}}(\lambda_2\sqrt{\theta})\\ &\times\left\{1-\frac{2}{3}\left[\frac{1}{6}-\frac{\mathrm{d}\ln\psi}{\mathrm{d}\ln\tau}\right]\left[\frac{\theta}{\tau}\right]+O([\theta/\tau]^2)\right\}\\ &-\frac{\lambda_2}{\sqrt{\pi}}\int_0^\theta\frac{(i_2/nFq)}{\sqrt{\theta-u}}\left\{1-\frac{1}{3}\left[\frac{\theta-u}{\tau}\right]+O([\theta/\tau]^2)\right\}\mathrm{d}u\end{aligned} \tag{25}$$

where $O([\theta/\tau]^2)$ denotes the sum of the second and higher order terms with respect to (θ/τ). Now, we expand (i_2/nFq) into a power series of $\sqrt{\theta/\tau}$. Thus

$$(i_2/nFq) = \phi_0+\phi_1+\phi_2+\phi_3+\cdots\cdots \tag{26}$$

where the function ϕ_j (j=0, 1, 2, 3, ⋯) corresponds to the order of $(\theta/\tau)^{\mathrm{j}/2}$. Substituting Eq. 26 into Eq. 25 and equating the coefficients of like powers of $\sqrt{\theta/\tau}$ yields the following set of integral equations:

$$\begin{aligned}\phi_0 &= \sqrt{D_\mathrm{O}}C_\mathrm{O}^\circ\left[\frac{1}{1+\exp(\zeta_2)}-\frac{1}{1+\exp(\zeta_1)}\right]\lambda_2\\ &+\left[\frac{i_1}{nFq}\right]\left[\frac{\lambda_2}{\lambda_1}\right]-\frac{\lambda_2}{\sqrt{\pi}}\int_0^\theta\frac{\phi_0(u)}{\sqrt{\theta-u}}\mathrm{d}u\end{aligned} \tag{27}$$

$$\phi_1 = \frac{2}{\sqrt{\pi}}\left[\frac{i_1}{nFq}\right](\lambda_2\sqrt{\tau})\sqrt{\theta/\tau}-\frac{\lambda_2}{\sqrt{\pi}}\int_0^\theta\frac{\phi_1(u)}{\sqrt{\theta-u}}\mathrm{d}u \tag{28}$$

$$\begin{aligned}\phi_2 &= \left[\frac{\lambda_2}{\lambda_1}\right]\left[\frac{i_1}{nFq}\right]\left[\frac{\mathrm{d}\ln\psi}{\mathrm{d}\ln\tau}\right]\left[\frac{\theta}{\tau}\right]+\frac{1}{3\tau}\frac{\lambda_2}{\sqrt{\pi}}\\ &\times\int_0^\theta\sqrt{\theta-u}\,\phi_0(u)\mathrm{d}u-\frac{\lambda_2}{\sqrt{\pi}}\int_0^\theta\frac{\phi_2(u)}{\sqrt{\theta-u}}\mathrm{d}u\end{aligned} \tag{29}$$

$$\begin{aligned}\phi_3 &= -\frac{4}{3\sqrt{\pi}}\left[\frac{i_1}{nFq}\right](\lambda_2\sqrt{\tau})\left[\frac{1}{6}-\frac{\mathrm{d}\ln\psi}{\mathrm{d}\ln\tau}\right](\theta/\tau)^{3/2}\\ &+\frac{1}{3\pi}\frac{2}{\sqrt{\pi}}\int_0^\theta\sqrt{\theta-u}\,\phi_1(u)\,\mathrm{d}u\\ &-\frac{\lambda_2}{\sqrt{\pi}}\int_0^\theta\frac{\phi_3(u)}{\sqrt{\theta-u}}\mathrm{d}u\end{aligned} \tag{30}$$

This set of integral equations can easily be solved by applying the method of Laplace transformation.[11] Thus, we obtain for (i_2/nFq), after performing some calculations,

$$\begin{aligned}(i_2/nFq) &= \frac{(i_\mathrm{d}^\mathrm{c})_\mathrm{Cott}}{nFq}\left[\frac{1}{1+\exp(\zeta_2)}-\frac{1}{1+\exp(\zeta_1)}\right]\Phi(\lambda_2\sqrt{\theta})\\ &\times\left\{1-\frac{1}{3}\left(\frac{\theta}{\tau}\right)\left[1+\frac{F_2(\lambda_2\sqrt{\theta})}{F_0(\lambda_2\sqrt{\theta})}\right]+O([\theta/\tau]^2)\right\}\\ &+\left[\frac{i_1(\tau)}{nFq(\tau)}\right]\{(\lambda_2/\lambda_1)-1\}F_0(\lambda_2\sqrt{\theta})\\ &\times\left\{1-\frac{1}{3}\left(\frac{\theta}{\tau}\right)\left[1+\frac{F_2(\lambda_2\sqrt{\theta})}{F_0(\lambda_2\sqrt{\theta})}\left(1+3\frac{\mathrm{d}\ln\psi}{\mathrm{d}\ln\tau}\right)\right]\right.\\ &\left.+O([\theta/\tau]^2)\right\}\\ &+\left[\frac{i_1(\tau)}{nFq(\tau)}\right]\left\{1+\left(\frac{\theta}{\tau}\right)\left[\frac{\mathrm{d}\ln\psi}{\mathrm{d}\ln\tau}\right]+O([\theta/\tau]^2)\right\}\end{aligned} \tag{31}$$

with

$$(i_d^c)_{Cott} = nFq(\tau+\theta)\sqrt{D_0}C_0^\circ/\sqrt{\pi\theta} \tag{32}$$

$$F_0(\xi) = \exp(\xi^2)\,\mathrm{erfc}(\xi) \tag{33}$$

$$F_2(\xi) = \xi^{-2}[1-(2/\sqrt{\pi})\,\xi - \exp(\xi^2)\mathrm{erfc}(\xi] \tag{34}$$

$$\Phi(\xi) = \sqrt{\pi}\,\xi\, F_0(\xi) = \sqrt{\pi}\,\xi \exp(\xi^2)\,\mathrm{erfc}(\xi) \tag{35}$$

where $(i_d^c)_{cott}$ denotes the diffusion current at the stationary plane electrode given by the Cottrell equation and erfc the complementary error function. The pulse polarographic current is in general measured as a difference between i_2 at $t=\tau+\theta_s$ (θ_s: sampling time) and i_1 at $t=\tau$. Therefore, taking into account the fact that the ratio of the surface area of DME at $t=\tau+\theta_s$ to that of $t=\tau$ can be expanded into the following power series of (θ_s/τ):

$$q(\tau+\theta_s)/q(\tau) = 1 + (2/3)(\theta_s/\tau) + O([\theta_s/\tau]^2), \tag{36}$$

we obtain for the pulse polarographic current, i_{pulse},

$$\begin{aligned} i_{pulse} &= i_2(\tau+\theta_s) - i_1(\tau) \\ &= (i_d^c)_{Cott}\left[\frac{1}{1+\exp(\zeta_2)}-\frac{1}{1+\exp(\zeta_1)}\right]\Phi(\lambda_2\sqrt{\theta_s}) \\ &\quad\times\left\{1-\frac{1}{3}\left[\frac{\theta_s}{\tau}\right]\left[1+\frac{F_2(\lambda_2\sqrt{\theta_s})}{F_0(\lambda_2\sqrt{\theta_s})}\right]+O([\theta_s/\tau]^2)\right\} \\ &\quad + i_1(\tau)\{(\lambda_2/\lambda_1) - 1\}F_0(\lambda_2\sqrt{\theta_s}) \\ &\quad\times\left\{1+\frac{1}{3}\left[\frac{\theta_s}{\tau}\right]\left[1-\frac{F_2(\lambda_2\sqrt{\theta_s})}{F_0(\lambda_2\sqrt{\theta_s})}\left(1+3\frac{\mathrm{d}\ln\psi}{\mathrm{d}\ln\tau}\right)\right]\right. \\ &\quad\left. + O([\theta_s/\tau]^2)\right\} \\ &\quad + i_1(\tau)\left\{\left[\frac{\theta_s}{\tau}\right]\left[\frac{2}{3}+\frac{\mathrm{d}\ln\psi}{\mathrm{d}\ln\tau}\right]+O([\theta_s/\tau]^2)\right\} \end{aligned} \tag{37}$$

In usual pulse polarographic practice, the values of τ and θ_s employed are of the orders of second and millisecond, respectively, *i.e.*, $\tau\simeq 1$—6 s and $\theta_s\simeq 1$—100 ms. Furthermore, the following relations hold in the whole range of the corresponding arguments:

$$-1\geqq\frac{F_2(\lambda_2\sqrt{\theta_s})}{F_0(\lambda_2\sqrt{\theta_s})}\geqq -2 \text{ and } 0\geqq\frac{\mathrm{d}\ln\psi(\lambda_1\sqrt{\tau})}{\mathrm{d}\ln\tau}\geqq-\frac{1}{2}.$$

Therefore, for $(\theta_s/\tau)\leqq 1/30$, which may be satisfied in usual experimental conditions, Eq. 37 can be greatly simplified, as follows:

$$\begin{aligned} i_{pulse} &= (i_d^c)_{Cott}\left[\frac{1}{1+\exp(\zeta_2)}-\frac{1}{1+\exp(\zeta_1)}\right]\Phi(\lambda_2\sqrt{\theta_s}) \\ &\quad + i_1(\tau)\{(\lambda_2/\lambda_1) - 1\}F_0(\lambda_2\sqrt{\theta_s}) \end{aligned} \tag{38}$$

This equation provides a general expression of the current-potential profiles for pulse polarography. Several modes of pulse polarography, nowadays practically used, are incorporated in this general equation. In the following, we shall further simplify Eq. 38 by introducing the experimental conditions corresponding to the mode employed.

Normal Pulse Polarography

In normal pulse polarography, the initial potential E_1 is anodic of the reduction wave and the scan of the potential E_2 is made to the cathodic direction. Therefore, we have $E_1\rightarrow$sufficiently more anodic potential than $E_{1/2}^r$. Thus

$$\zeta_1 \longrightarrow +\infty,\ \lambda_1 \longrightarrow +\infty \text{ and } i_1(\tau)\longrightarrow 0.$$

Introducing the above conditions into Eq. 38 yields

$$i_{n\text{-pulse}}^c = \frac{(i_d^c)_{Cott}}{1+\exp(\zeta_2)}\Phi(\lambda_2\sqrt{\theta_s}) \tag{39}$$

where $i_{n\text{-pulse}}^c$ denotes the normal pulse polarographic current. This is the general equation of current-potential curves for normal pulse polarography. For the variations of current-potential curves with the kinetic parameters of electrode reaction, see Fig. 1. Equation 39 is exactly the same as derived by a number of authors[12] for the potentiostatic experiments at the stationary plane electrode. In the potentiostatic method, the variation of faradaic current with time at a constant potential is examined, whereas in pulse polarography the faradaic current at a given time θ_s is measured as a function of the electrode potential. Therefore, in order to examine the behavior of pulse polarographic waves, it is convenient to derive the expression similar to the log-plot in d.c. polarography.

First, consider the limiting case of reversible waves. The function $\Phi(\xi)$ is equal to unity within an error of 2%, when $\xi\geqq 5$. Therefore, if the condition

$$(k_0\sqrt{\theta_s}/\sqrt{D}) \geqq 5\times\alpha^\alpha(1-\alpha)^{1-\alpha} \tag{40}$$

is satisfied, Eq. 39 can be simplified into

$$i_{n\text{-pulse}}^c = (i_d^c)_{Cott}/[1+\exp(\zeta_2)] \tag{41a}$$

or solving the above equation with respect to E_2 yields

$$E_2 = E_{1/2}^r - (RT/nF)\ln[x/(1-x)] \tag{41b}$$

with

$$x = i_{n\text{-pulse}}^c/(i_d^c)_{Cott} \tag{42}$$

This is the equation for the log-plot of reversible waves, which is of the same form as for d.c. polarography.

Next, consider the case, $(k_0\sqrt{\theta_s}/\sqrt{D})\leqq 5\times\alpha^\alpha(1-\alpha)^{1-\alpha}$, in which the irreversibility appears in the pulse polarograms. Fortunately, Oldham and Parry[13] derived the convenient approximate equation for the inverse function of $\Phi(\xi)$, as follows:

$$\xi = \frac{\sqrt{3}}{4}\left\{\frac{1.75+\Phi^2}{1-\Phi}\right\}^{1/2}\Phi \tag{43}$$

Therefore, after combining Eq. 39 with Eq. 43 and performing some rearrangements, we obtain

$$E_2 = E^* - \frac{RT}{\alpha nF}\ln\left\{x\left[\frac{1.75+x^2(1+\exp\zeta_2)^2}{1-x(1+\exp\zeta_2)}\right]^{1/2}\right\} \tag{44}$$

with

$$E^* = E_{1/2}^r + \frac{RT}{\alpha nF}\ln\left[\frac{4}{\sqrt{3}}\frac{k_0\sqrt{\theta_s}}{\sqrt{D}}\right] \tag{45}$$

Equation 44 suggests a new log-plot for the normal pulse polarographic waves.

Now consider the pulse-polarographically quasi-reversible waves, for which the condition

$$5\times\alpha^\alpha(1-\alpha)^{1-\alpha}\geqq(k_0\sqrt{\theta_s}/\sqrt{D})\geqq\exp[-4(1+\alpha)] \tag{46}$$

is satisfied. In general, the d.c. polarographic wave exhibits higher reversibility than the corresponding pulse polarographic wave does, because of the difference in electrolysis time scales employed in two methods. Therefore, from the analysis of d.c. polarographic wave corresponding to the pulse-polarographically quasi-reversible wave, we can determine the reversible half-wave potential $E^{\mathrm{r}}_{1/2}$ by using the extrapolation methods.[14,15] Then, the log-term in Eq. 44 becomes the experimentally accessible quantity. Thus, if we plot $\log (x[\{1.75+x^2(1+\exp\zeta_2)^2\}/\{1-x(1+\exp\zeta_2)\}]^{1/2})$ against E_2, we obtain a straight line, which has the reciprocal slope of $(2.3RT/\alpha nF)$ and intersects with the zero-line at $E_2=E^*$, provided that the transfer coefficient α may be regarded as constant in the potential region concerned. Therefore, we can determine the kinetic parameters of electrode reaction from the values of the reciprocal slope and of the potential E^*.

For the irreversible waves, which satisfy the condition

$$(k_0\sqrt{\theta_s}/\sqrt{D}) \leqq \exp[-4(1+\alpha)], \tag{47}$$

the term $\exp(\zeta_2)$ in Eq. 44 can be neglected compared with unity in the whole potential region concerned. Therefore, Eq. 44 can be reduced to

$$E_2 = E^* - \frac{RT}{\alpha nF}\ln\left\{x\left(\frac{1.75+x^2}{1-x}\right)^{1/2}\right\} \tag{48}$$

where E^* is the half-wave potential of irreversible wave. This is the same equation as that previously proposed by Oldham and Parry[13] for totally irreversible waves. Equation 48 indicates that the plot of $\log [x\{(1.75+x^2)/(1-x)\}^{1/2}]$ *vs.* E_2 can be made without any knowledge of $E^{\mathrm{r}}_{1/2}$ and thus the kinetic parameters of electrode reaction can be determined from this plot in the same way as described above.

According to the modern theory of electron transfer at electrodes,[16] it is shown that the transfer coefficient may depend on the electrode potential. In such cases, it is better to rewrite Eq. 44 as

$$\ln \vec{k}_2 = -\ln\left[\frac{4}{\sqrt{3}}\frac{\sqrt{\theta_s}}{\sqrt{D_0}}\right] + \ln\left\{x\left[\frac{1.75+x^2(1+\exp\zeta_2)^2}{1-x(1+\exp\zeta_2)}\right]^{1/2}\right\} \tag{49}$$

which can be derived from Eq. 44 by taking into account the relations given by Eqs. 5, 9, and 10. Equation 49 indicates that the plot of $\log (x[\{1.75+x^2(1+\exp\zeta_2)^2\}/\{1-x(1+\exp\zeta_2)\}]^{1/2})$ *vs.* E_2 manifests the potential dependence of the cathodic rate constant $\vec{k}_2$. Thus, this log-plot may appear as bent toward the potential axis, if the transfer coefficient shows such a potential dependence as predicted by the modern theory of electron transfer at electrodes.[17]

Scan-reversal Pulse Polarography

In order to examine the reversibility of electrode reactions, Oldham and Parry[18] presented the scan-reversal pulse polarographic technique and discussed two limiting cases, *i.e.*, the behavior of reversible and totally irreversible waves. Since the general case is incorporated in Eq. 38, we shall derive a general equation for the scan-reversal pulse polarographic current, $i^{\mathrm{a}}_{\text{r-pulse}}$.

In scan-reversal pulse polarography, the initial potential E_1 is set on the cathodic diffusion current plateau and the potential E_2 is scanned from the cathodic plateau to the anodic direction. Hence we have

$$E_1 \longrightarrow \text{sufficiently more cathodic potential than } E^{\mathrm{r}}_{1/2}.$$

Thus

$$\zeta_1 \longrightarrow -\infty,\ \lambda_1 \longrightarrow +\infty \text{ and } i_1(\tau) \longrightarrow (i^{\mathrm{c}}_{\mathrm{d}})_{\mathrm{Ilk}}.$$

Substituting the above conditions into Eq. 38 yields

$$i^{\mathrm{a}}_{\text{r-pulsd}} = -\frac{(i^{\mathrm{c}}_{\mathrm{d}})_{\mathrm{Cott}}}{1+\exp(-\zeta_2)}\Phi(\lambda_2\sqrt{\theta_s}) - (i^{\mathrm{c}}_{\mathrm{d}})_{\mathrm{Ilk}}F_0(\lambda_2\sqrt{\theta_s}) \tag{50}$$

This is the general expression of current-potential curves in scan-reversal pulse polarography. The first term on the right hand side of Eq. 50 manifests the anodic normal pulse polarographic wave, as can readily be seen from the comparison with Eq. 39, whereas the second term indicates the effects of the pre-electrolysis at the potential corresponding to the cathodic diffusion current plateau during the period 0—τ.

In order to visualize the variations of wave-shapes in dependence of the kinetic parameters of electrode reaction, the normalized current-potential curves, *i.e.*, $i^{\mathrm{a}}_{\text{r-pulse}}/(i^{\mathrm{c}}_{\mathrm{d}})_{\mathrm{Cott}}$ *vs.* E_2 curves, were calculated numerically for a series of values of $(k_0\sqrt{\theta_s}/\sqrt{D})$ under the assumption that $n=2$, $\alpha=0.5$, $\theta_s/\tau=0.01$ and $T=25$ °C. The results obtained are shown in Fig. 1, in which the cathodic normal pulse polarographic waves are also given for comparison.

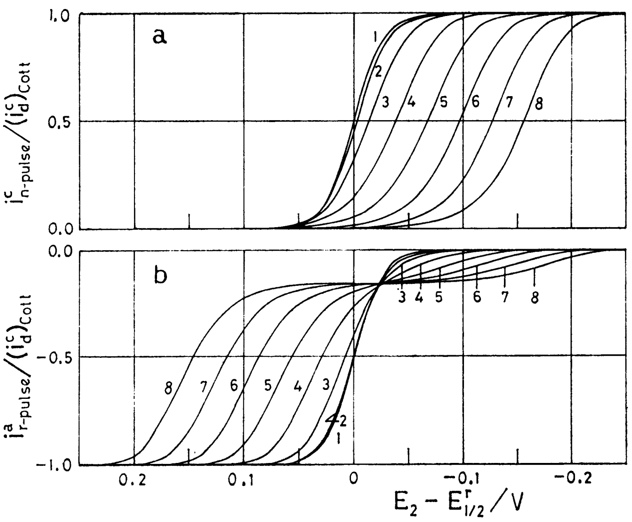

Fig. 1. Current-potential curves of normal pulse and scan-reversal pulse polarography.
(a) Normal, (b) scan-reversal. Values of $\log(\overline{k_0\sqrt{\theta_0}}/\sqrt{D})$: (1)$\geqq$0.5 (reversible), (2) 0.0, (3) −0.5, (4) −1.0, (5) −1.5, (6) −2.0, (7) −2.5, (8) −3.0.

In the following, we shall examine the general Eq. 50. First, consider the reversible case, in which the condition (40) is fulfilled. In this case, the function $\Phi(\lambda_2\sqrt{\theta_s})$ in the first term on the right hand side of Eq. 50 is reduced to unity and the second term can be neglected within an error of *ca.* 3%. Hence we have for the reversible waves of scan-reversal pulse polarography

$$i^{\mathrm{a}}_{\text{r-pulse}} = -(i^{\mathrm{c}}_{\mathrm{d}})_{\mathrm{Cott}}/[1+\exp(-\zeta_2)] \tag{51}$$

Equation 51 indicates that the reversible scan-reversal pulse polarographic wave has the same wave-height and the same half-wave potential as the reversible normal pulse polarographic wave does.

When values of the parameter $(k_0\sqrt{\theta_s}/\sqrt{D})$ are decreased, both the irreversibility and the effect of the second term on the right hand side of Eq. 50 appear and hence the portions of the wave, which are lower than or higher than $(i_d^c)_{\text{Ilk}}$, shift toward the more cathodic or the more anodic potential, respectively, as can readily be seen from Fig. 1. Thus the wave appears to have a drawn-out shape. Finally, when values of $(k_0\sqrt{\theta_s}/\sqrt{D})$ become so small that the condition (47) is fulfilled, the wave splits definitely into two waves. This behavior of the wave can readily be understood if recalling the fact that the pulse polarographic current is measured as the difference between the currents before and after the pulse application. Thus, the first wave does not correspond to the true anodic process but to the cathodic one, and in the potential region of the second wave occurs the anodic process.

Now such irreversible cases will be examined in some detail. The first and second waves appear at the potentials sufficiently more cathodic and more anodic than $E_{1/2}^r$, respectively, so that in the potential region corresponding to the first wave Eq. 50 can be reduced to

$$i_{\text{r-pulse}}^a = -(i_d^c)_{\text{Ilk}}F_0(\lambda_2\sqrt{\theta_s}) \tag{52}$$

This is the equation for the current-potential curve of the first wave. When the potential E_2 is placed near $E_{1/2}^r$, the values of $(\lambda_2\sqrt{\theta_s})$ become very small and thus the function $F_0(\lambda_2\sqrt{\theta_s})$ approarches to unity. Hence the limiting current of the first wave, $(i_l^a)_{\text{1st}}$, can be given by

$$(i_l^a)_{\text{1st}} = -(i_d^c)_{\text{Ilk}}. \tag{53}$$

This equation indicates that the height of the first wave is equal to that of d.c. polarographic wave, expressed by the Ilkovic equation. The half-wave potential of the first wave $(E_{1/2}^a)_{\text{1st}}$, can be obtained by equating $i_{\text{r-pulse}}^a$ to $-(1/2)(i_d^c)_{\text{Ilk}}$. Thus, by recalling the facts that the function $F_0(\xi)$ is equal to 1/2 at $\xi=0.770$ and that in this potential region $(\lambda_2\sqrt{\theta_s})$ can be written as $(k_0\sqrt{\theta_s}/\sqrt{D})$ exp $[-(\alpha nF/RT)(E_2-E_{1/2}^r)]$, we have

$$(E_{1/2}^a)_{\text{1st}} = E_{1/2}^r + \frac{RT}{\alpha nF}\ln[1.30\,(k_0\sqrt{\theta_s}/\sqrt{D})] \tag{54}$$

Hence the half-wave potential of the first wave shifts toward the cathodic direction with decreasing values of $(k_0\sqrt{\theta_s}/\sqrt{D})$. On the other hand, the potential region corresponding to the second wave is sufficiently more anodic than $E_{1/2}^r$, so that Eq. 50 can be reduced to

$$i_{\text{r-pulse}}^a = -(i_d^c)_{\text{Cott}}\Phi(\lambda_2'\sqrt{\theta_s}) - (i_d^c)_{\text{Ilk}}F_0(\lambda_2'\sqrt{\theta_s}) \tag{55}$$

with

$$\lambda_2'\sqrt{\theta_s} = (k_0\sqrt{\theta_s}/\sqrt{D}) \times \exp[\{(1-\alpha)\,nF/RT\}(E_2-E_{1/2}^r)] \tag{56}$$

where it should be kept in mind that $i_{\text{r-pulse}}^a$ in Eq. 50 denotes the total anodic current measured from the zero-line. If the current of the second wave is measured from the limiting current plateau of the first wave, we may write the equation for the current-potential curves of the second wave, as follows:

$$(i_{\text{r-pulse}}^a)_{\text{2nd}} = -(i_d^c)_{\text{Cott}}\Phi(\lambda_2'\sqrt{\theta_s}) + (i_d^c)_{\text{Ilk}}[1-F_0(\lambda_2'\sqrt{\theta_s})] \tag{57}$$

The limiting current of the second wave, $(i_l^a)_{\text{2nd}}$, can be derived by inserting the condition (nF/RT) $(E_2-E_r^{1/2})\to+\infty$ into Eq. 57. Hence

$$(i_l^a)_{\text{2nd}} = -[(i_d^c)_{\text{Cott}} - (i_d^c)_{\text{Ilk}}]. \tag{58}$$

The half-wave potential of the second wave, $(E_{1/2}^a)_{\text{2nd}}$, may be obtained by substituting the condition $(i_{\text{r-pulse}}^a)_{\text{2nd}}=(1/2)(i_l^a)_{\text{2nd}}$ into Eq. 57. Thus, we have, after performing some rearrangements,

$$[1-2\Phi(\gamma)]/[2F_0(\gamma)-1] = (i_d^c)_{\text{Ilk}}/(i_d^c)_{\text{Cott}} \tag{59}$$

with

$$\gamma = (k_0\sqrt{\theta_s}/\sqrt{D})\exp[\{(1-\alpha)nF/RT\} \times \{(E_{1/2}^a)_{\text{2nd}} - E_{1/2}^r\}] \tag{60}$$

The values of γ, which satisfy Eq. 59, may be calculated numerically as a function of $[(i_d^c)_{\text{Ilk}}/(i_d^c)_{\text{Cott}}]$. Since $(\theta_s/\tau)<1/30$ for usual pulse polarographic conditions, numerical calculations were performed for the range:

$$0 < (i_d^c)_{\text{Ilk}}/(i_d^c)_{\text{Cott}} < 0.3$$

The results obtained indicates that γ can be expressed by the following equation within errors of ±0.001 in the absolute values of γ:

$$\gamma = 0.433 - 0.205\,[(i_d^c)_{\text{Ilk}}/(i_d^c)_{\text{Cott}}] - 0.16\,[(i_d^c)_{\text{Ilk}}/(i_d^c)_{\text{Cott}}]^2 \tag{61}$$

Taking the logarithms of both sides of Eq. 60 yields for the half-wave potential of the second wave

$$(E_{1/2}^a)_{\text{2nd}} = E_{1/2}^r - \frac{RT}{(1-\alpha)nF}\ln[(1/\gamma)(k_0\sqrt{\theta_s}/\sqrt{D})], \tag{62}$$

where γ is given by Eq. 61. Hence, the half-wave potential of the second wave shifts toward the anodic direction with decreasing values of $(k_0\sqrt{\theta_s}/\sqrt{D})$.

Comparison of Eq. 58 with Eq. 53 yields for the ratio of the height of the first wave to that of the second wave

$$(i_l^a)_{\text{1st}}/(i_l^a)_{\text{2nd}} = (i_d^c)_{\text{Ilk}}/[(i_d^c)_{\text{Cott}} - (i_d^c)_{\text{Ilk}}] = 1/[\sqrt{(3/7)(\tau/\theta_s)}-1] \tag{63}$$

Thus, for usual pulse polarographic conditions, *i.e.*, $(\tau/\theta_s)\sim100$, we have $(i_l^a)_{\text{1st}} : (i_l^a)_{\text{2nd}}\approx1:6$. Further, the difference between the half-wave potentials of the first and second waves can be obtained from Eqs. 54 and 62, as follows:

$$(E_{1/2}^a)_{\text{2nd}} - (E_{1/2}^a)_{\text{1st}} = -\frac{RT}{\alpha(1-\alpha)nF}\ln\left[\frac{1.30^{1-\alpha}}{\gamma^{\alpha}}\,\frac{k_0\sqrt{\theta_s}}{\sqrt{D}}\right] \tag{64}$$

Equation 64 indicates that the difference between two half-wave potentials is increased with decreasing values of $(k_0\sqrt{\theta_s}/\sqrt{D})$ and thus it can be employed as an index indicating the degree of irreversibility of the electrode reaction concerned.

Differential Pulse Polarography

In differential pulse polarography, both the potentials E_1 and E_2 are scanned simultaneously toward the cathodic direction with their difference, $E_1-E_2\equiv\Delta E$, being kept constant. Hence, after performing some calculations by taking into account Eqs. 15, 17, 32, and 35, Eq. 38 can be transformed into

$$i_{\text{dif-pulse}} = (i_d^c)_{\text{Cott}} \frac{\sinh(\Delta\zeta/2)}{\cosh(\zeta_m)+\cosh(\Delta\zeta/2)} F_{\text{dcp}}\,\Phi(\lambda_2\sqrt{\theta_s}) \tag{65}$$

with

$$F_{\text{dcp}} = 1 + \frac{\exp(-\zeta_m)\sinh(\alpha\Delta\zeta/2)-\sinh([1-\alpha]\Delta\zeta/2)}{\exp(\alpha\Delta\zeta/2)\sinh(\Delta\zeta/2)} \times \psi(\lambda_1\sqrt{\tau}) \tag{66}$$

$$\Delta\zeta = \zeta_1 - \zeta_2 = (nF/RT)(E_1 - E_2) = (nF/RT)\Delta E \tag{67}$$

$$\zeta_m = (\zeta_1 + \zeta_2)/2 = (nF/RT)(E_m - E_{1/2}^r) \tag{68}$$

$$E_m = (E_1 + E_2)/2 = E_1 - (\Delta E/2) \tag{69}$$

where $\psi(\lambda_1\sqrt{\tau})$ is defined by Eq. 16 and can be evaluated with sufficient accuracy by using the approximate Eq. 18. Further it should be noticed that the potential E_m defined by Eq. 69 is by $(\Delta E/2)$ more negative than the potential E_1 which is frequently employed as the potential axis of differential pulse polarograms. Equation 65 is the general expression for the differential pulse polarographic waves, which holds for any values of the pulse height ΔE. If ΔE is smaller than *ca.* $5/n$ mV, Eq. 65 can be simplified into

$$i_{\text{dif-pulse}} = \frac{(i_d^c)_{\text{Cott}}\Delta\zeta}{4\cosh^2(\zeta_m/2)} F_{\text{dcp}}\Phi(\lambda_m\sqrt{\theta_s}) \tag{70}$$

with

$$F_{\text{dcp}} = 1 + [\alpha\exp(-\zeta_m) - (1-\alpha)]\psi(\lambda_m\sqrt{\tau}) \tag{71}$$

$$\lambda_m = (k_0/\sqrt{D})[\exp(-\alpha\zeta_m) + \exp\{(1-\alpha)\zeta_m\}] \tag{72}$$

In order to visualize the behavior of differential pulse polarographic waves in dependence of the kinetic parameters of electrode reaction, numerical calculations using the general Eq. 65 were performed for a series of values of $(k_0\sqrt{\theta_s}/\sqrt{D})$ and α under the assumption that $n=2$, $\Delta E=10$ mV, $\theta_s/\tau=0.01$ and $T=25$ °C. In Fig. 2, the normalized differential pulse polarographic currents obtained for $\alpha=0.5$ and 0.3 are plotted against the potential E_m. It can be seen from Fig. 2 that the $i_{\text{dif-pulse}}$—E_m curves have generally one peak, but when $\alpha<0.5$ and $(k_0\sqrt{\theta_s}/\sqrt{D})\approx0.1-0.02$, they show some anomaly, *i.e.*, they have a shoulder or two peaks, as can be seen from the curves 4, 5, and 6 in Fig. 2(b). Further, we can see that the peak currents decrease at first very rapidly with decreasing the value of $(k_0\sqrt{\theta_s}/\sqrt{D})$ and then approach to a limiting value which does not depend on the standard rate constant k_0 (see Eq. 88). This behavior of differential pulse polarographic waves in dependence of the kinetic parameters is quite similar to that of square wave polarographic waves, which are given in Fig. 3 of Ref. 19.

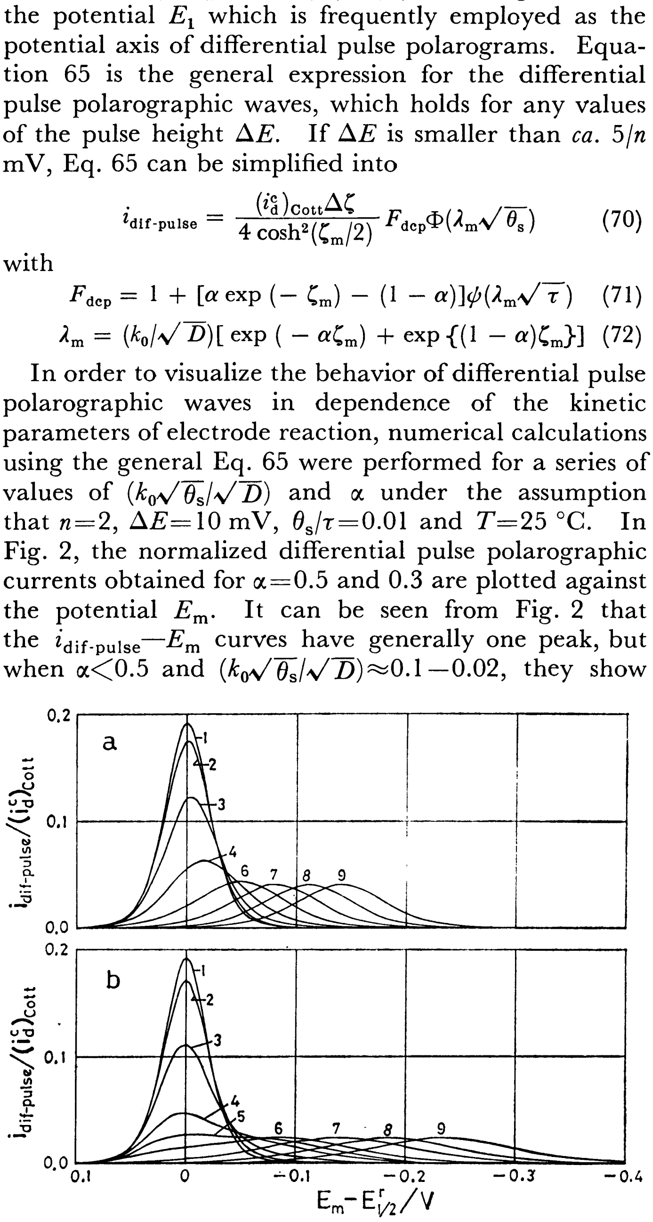

Fig. 2. Current-potential curves of differential pulse polarography.
(a) $\alpha=0.5$, (b) $\alpha=0.3$. Values of log $(k_0\sqrt{\theta_s}/\sqrt{D})$: (1)$\geqq$0.5 (reversible), (2) 0.0, (3) −0.5, (4) −1.0, (5) −1.25, (6) −1.5, (7) −2.0, (8) −2.5, (9) −3.0.

In the following, we shall examine the two limiting cases in some detail. First, consider the reversible limiting case, in which the condition (40) is fulfilled. In this case, the functions F_{dcp} and $\Phi(\lambda_2\sqrt{\theta_s})$ both approarch to unity. Hence Eq. 65 can be reduced to

$$i_{\text{dif-pulse}} = (i_d^c)_{\text{Cott}} \frac{\sinh(\Delta\zeta/2)}{\cosh(\zeta_m)+\cosh(\Delta\zeta/2)}. \tag{73}$$

This is the equation for the reversible waves of differential pulse polarography, which should be compared with Eq. 75 or 76 of Ref. 7 for the reversible square wave polarographic waves. Now we determine the three parameters which characterize the wave-shape, *i.e.*, the peak potential $(E_m)_p$, the peak current $(i_{\text{dif-pulse}})_p$ and the half-peak width $\Delta(E_m)_{p/2}$. As can easily be seen from Eq. 73, a maximum appears at $\zeta_m=0$. Hence, the peak potential can be given by

$$(E_m)_p = E_{1/2}^r. \tag{74}$$

Thus the peak potential coinsides with the reversible half-wave potential. The peak current can be derived by inserting Eq. 74 into Eq. 73, as follows:

$$(i_{\text{dif-pulse}})_p = (i_d^c)_{\text{Cott}}\tanh(\Delta\zeta/4) = (i_d^c)_{\text{Cott}}\tanh(nF\Delta E/4RT) \tag{75}$$

Equation 75 reveals that the normalized peak current, $(i_{\text{dif-pulse}})_p/(i_d^c)_{\text{Cott}}$, is increased in proportion to the pulse height ΔE for $(nF\Delta E/RT)<1$ and it approarches to the limiting value of unity when $(nF\Delta E/RT)>10$. The half-peak width can be defined as the difference between two potentials which satisfy the condition:

$$i_{\text{dif-pulse}} = (1/2)(i_{\text{dif-pulse}})_p.$$

Thus, introducing Eqs. 73 and 75 into the above condition and performing some calculations yields for such potentials

$$(E_m)_{p/2} = E^r{}_{1/2} \pm (RT/nF) \times\cosh^{-1}[2 + \cosh(nF\Delta E/2RT)]. \tag{76}$$

Hence the half-peak width $\Delta(E_m)_{p/2}$ can be expressed as

$$\Delta(E_m)_{p/2} = (2RT/nF) \times\cosh^{-1}[2 + \cosh(nF\Delta E/2RT)]. \tag{77}$$

For $(nF\Delta E/RT)<0.8$, Eq. 77 can be reduced to

$$\Delta(E_m)_{p/2} = 3.53(RT/nF), \tag{78}$$

On the other hand, when $(nF\Delta E/RT)>8$, we have

$$\Delta(E_m)_{p/2} = \Delta E \tag{79}$$

Equations 78 and 79 indicate that the half-peak width has the constant value of $90/n$ mV at 25 °C when $\Delta E<20/n$ mV, whereas it becomes to be equal to the pulse height ΔE for $\Delta E>200/n$ mV.

Next, consider another limiting case, in which the condition:

$$(k_0\sqrt{\tau}/\sqrt{D}) \leqq \exp[-4(1+\alpha)] \tag{80}$$

is fulfilled. In this case, the electrode process becomes d.c. polarographically irreversible[9] and thus, of course, pulse-polarographically irreversible. Then the corresponding wave appears in the potential region sufficiently more cathodic than $E^{\mathrm{r}}_{1/2}$. Therefore, the general Eq. 65 can be transformed into

$$i_{\mathrm{dif\text{-}pulse}} = (i^{\mathrm{c}}_{\mathrm{d}})_{\mathrm{Cott}}[1-\exp(-\alpha\Delta\zeta)]\psi(\kappa^{-1}\chi)\Phi(\kappa\chi) \tag{81}$$

where κ and χ are defined as

$$\kappa = \sqrt[4]{\theta_{\mathrm{s}}/\tau}\,\exp(\alpha\Delta\zeta/2) \tag{82}$$

$$\chi = (k_0\,\sqrt[4]{\theta_{\mathrm{s}}\tau}/\sqrt{D})\exp(-\alpha\zeta_{\mathrm{m}}) \tag{83}$$

Equation 81 provides the expression of irreversible waves. We shall now derive the equations for the peak potential, the peak current and the half-peak width of irreversible waves. As can be seen from Eqs. 81—83, the dependence of $i_{\mathrm{dif\text{-}pulse}}$ on E_{m} can be given by $\psi(\kappa^{-1}\chi)\Phi(\kappa\chi)$ *vs.* $\ln\chi$ curves. Thus, the values of $\psi(\kappa^{-1}\chi)\Phi(\kappa\chi)$ in dependence of $\ln\chi$ were numerically calculated for a series of values of κ. The results obtained for the range of $0.1<\kappa<30$ are summarized as follows:

(1) The values of $\ln\chi_{\mathrm{p}}$, at which $\psi(\kappa^{-1}\chi)\Phi(\kappa\chi)$ shows a maximum, can be given by

$$\ln\chi_{\mathrm{p}} = -0.27-0.40\,\mathrm{sech}(2.2-0.8\ln\kappa) \tag{84}$$

(2) The maximum values of $\psi\Phi$, *i.e.*, $\psi(\kappa^{-1}\chi_{\mathrm{p}})\Phi(\kappa\chi_{\mathrm{p}})$, can be given by

$$\psi(\kappa^{-1}\chi_{\mathrm{p}})\Phi(\kappa\chi_{\mathrm{p}}) = \frac{(\ln\kappa)^{1.62}}{1.50+(\ln\kappa)^{1.62}} \tag{85}$$

(3) The difference between the two values of $\ln\chi$, $\ln\chi'_{\mathrm{p}/2}$ and $\ln\chi''_{\mathrm{p}/2}$, which satisfy the algebraic equation:

$$\psi(\kappa^{-1}\chi)\Phi(\kappa\chi) = (1/2)\psi(\kappa^{-1}\chi_{\mathrm{p}})\Phi(\kappa\chi_{\mathrm{p}}),$$

can be given by

$$\Delta\ln\chi_{\mathrm{p}/2} = \ln\chi'_{\mathrm{p}/2} - \ln\chi''_{\mathrm{p}/2} = 3.21+0.522\,|\ln\kappa|^{1.77} \tag{86}$$

Equations 84—86 hold with errors of less than 2%. Therefore, by taking into account Eqs. 81—86, we obtain the following equations for the peak potential, the peak current and the half-peak width of the irreversible wave:

$$\begin{aligned}(E_{\mathrm{m}})_{\mathrm{p}} = E^{\mathrm{r}}_{1/2} + (RT/\alpha nF)\{&\ln(k_0\sqrt[4]{\theta_{\mathrm{s}}\tau}/\sqrt{D})+0.27\\ &+0.40\,\mathrm{sech}[2.2-0.2\ln(\theta_{\mathrm{s}}/\tau)\\ &-0.4(\alpha nF/RT)\Delta E]\}\end{aligned} \tag{87}$$

$$\begin{aligned}(i_{\mathrm{dif\text{-}pulse}})_{\mathrm{p}} = {}&(i^{\mathrm{c}}_{\mathrm{d}})_{\mathrm{Cott}}[1-\exp\{-(\alpha nF/RT)\Delta E\}]\\ &\times\frac{[(\alpha nF/2RT)\Delta E+(1/4)\ln(\theta_{\mathrm{s}}/\tau)]^{1.62}}{1.50+[(\alpha nF/2RT)\Delta E+(1/4)\ln(\theta_{\mathrm{s}}/\tau)]^{1.62}}\end{aligned} \tag{88}$$

$$\begin{aligned}\Delta(E_{\mathrm{m}})_{\mathrm{p}/2} = {}&(RT/\alpha nF)\{3.21\\ &+0.522|(\alpha nF/2RT)\Delta E+(1/4)\ln(\theta_{\mathrm{s}}/\tau)|^{1.77}\}\end{aligned} \tag{89}$$

From Eqs. 87—89 we can readily see how the shape of irreversible waves varys in dependence of the kinetic parameters of electrode reaction. The standard rate constant k_0 is not contained in the equations of the peak current and the half-peak width and hence it has no influence on the shape of irreversible waves, while the peak potential shifts in proportion to $\ln k_0$. On the other hand, the transfer coefficient α has a great influence both on the wave-shape and the peak potential in somewhat complicated ways, as can be seen from Eqs. 87—89.

Remark for Applying the Theory to Analysis of Experimental Data

In the pulse polarographic practice, in order to increase the S/N ratio, the pulse polarographic current is frequently integrated over some short period, $\Delta\theta$, at the end of the pulse duration, and it is expressed as the value averaged over $\Delta\theta$. In the theoretical considerations developed above, however, it is the instantaneous value at $\theta=\theta_{\mathrm{s}}$. Thus, one problem may arise: what magnitude of error is introduced when the instantaneous value at $\theta=\theta_{\mathrm{s}}$ is replaced by the value averaged over the time-duration from $\theta_{\mathrm{s}}-(1/2)\Delta\theta$ to $\theta_{\mathrm{s}}+(1/2)\Delta\theta$? If the current may vary linearly with time, the average current is precisely equal to the instantaneous one at the middle point of the time duration concerned. The case, in which the variation of current with time most greatly deviates from the linearity, is that of reversible waves. As can be seen from Eqs. 32, 41a, 51, and 73, the pulse polarographic current of reversible waves is proportional to $1/\sqrt{\theta}$. Therefore, the current, $\bar{i}_{\mathrm{pulse}}$, averaged over the time-duration from $\theta_{\mathrm{s}}-(\Delta\theta/2)$ to $\theta_{\mathrm{s}}+(\Delta\theta/2)$ is given by

$$\begin{aligned}\bar{i}_{\mathrm{pulse}} &= \mathrm{const.}\frac{1}{\Delta\theta}\int_{\theta_{\mathrm{s}}-\Delta\theta/2}^{\theta_{\mathrm{s}}+\Delta\theta/2}\mathrm{d}\theta/\sqrt{\theta}\\ &= \mathrm{const.}\frac{2\sqrt{\theta_{\mathrm{s}}}}{\Delta\theta}\left\{\left[1+\frac{\Delta\theta}{2\theta_{\mathrm{s}}}\right]^{1/2}-\left[1-\frac{\Delta\theta}{2\theta_{\mathrm{s}}}\right]^{1/2}\right\}\end{aligned}$$

For $\Delta\theta/2\theta_{\mathrm{s}}<1$, we have

$$\bar{i}_{\mathrm{pulse}} = \mathrm{const.}\frac{1}{\sqrt{\theta_{\mathrm{s}}}}\left\{1+\frac{1}{8}\left[\frac{\Delta\theta}{2\theta_{\mathrm{s}}}\right]^2+\frac{7}{128}\left[\frac{\Delta\theta}{2\theta_{\mathrm{s}}}\right]^4+\cdots\right\}$$

On the other hand, the instantaneous value of the pulse polarographic current at $\theta=\theta_{\mathrm{s}}$ is given by

$$i_{\mathrm{pulse}}(\theta=\theta_{\mathrm{s}}) = \mathrm{const.}\,(1/\sqrt{\theta_{\mathrm{s}}})$$

Hence

$$\left|\frac{i_{\mathrm{pulse}}(\theta=\theta_{\mathrm{s}})-\bar{i}_{\mathrm{pulse}}}{i_{\mathrm{pulse}}(\theta=\theta_{\mathrm{s}})}\right| = \frac{1}{8}\left[\frac{\Delta\theta}{2\theta_{\mathrm{s}}}\right]^2\left\{1+\frac{7}{16}\left[\frac{\Delta\theta}{2\theta_{\mathrm{s}}}\right]^2+\cdots\right\} \tag{90}$$

Equation 90 reveals that when the condition:

$$\Delta\theta/\theta_{\mathrm{s}} \leqq 1/2 \tag{91}$$

is satisfied, the average current is equal to the instantaneous one at the middle point of the integration range with errors of less than 1%. This statement holds well also for the quasi-reversible and irreversible waves. Hence, we can derive the following conclusion: Let the current be integrated over the time-duration from θ_1 to $\theta_1+\Delta\theta$. Then θ_1 should be selected to be larger than $(3/2)\Delta\theta$, and in such a case the average value may be replaced by the instantaneous one at $\theta=\theta_1+(\Delta\theta/2)$.

Appendix

In this appendix, the integrals I_1 and I_2 will be evaluated. Introducing Eq. 15 with Eq. 16a into Eq. 21 yields

$$I_1 = \frac{\sqrt{D_O}C_O^\circ}{1+\exp(\zeta_1)} \lambda_1 \sum_{\nu=0}^{\infty} (-1)^\nu a_\nu (\sqrt{3/7}\,\lambda_1)^\nu \times \int_0^\tau \frac{u^{(3\nu+4)/6}\mathrm{d}u}{\sqrt{(\tau+\theta)^{7/3}-u^{7/3}}} \quad \text{(A-1)}$$

Substituting $u=(\tau+\theta)\ v^{3/7}$ into the above equation and performing the indicated integration, we obtain

$$I_1 = \sqrt{\frac{3}{7}} \frac{\sqrt{D_O}C_O^\circ}{1+\exp(\zeta_1)} \sum_{\nu=0}^{\infty} (-1)^\nu a_\nu (\sqrt{3/7}\,\lambda_1\sqrt{\tau+\theta})^{\nu+1} \times \left\{ \frac{\sqrt{\pi}\,\Gamma([3\nu+10]/14)}{\Gamma([3\nu+17]/14)} - B\left[1-(1+[\theta/\tau])^{-7/3};\ \frac{1}{2}, \frac{3\nu+10}{14}\right] \right\} \quad \text{(A-2)}$$

where $B\ (\xi;\ a,\ b)$ is the incomplete beta function, defined by

$$B(\xi;a,b) = \int_0^\xi \xi^{a-1}(1-\xi)^{b-1}\mathrm{d}\xi$$

Taking into account Eqs. 16a, 16b, and 17, we obtain

$$I_1 = \sqrt{\frac{3\pi}{7}} \frac{\sqrt{D_O}C_O^\circ}{1+\exp(\zeta_1)} \left\{ 1 - \psi(\lambda_1\sqrt{\tau+\theta}) - \frac{1}{\sqrt{\pi}} \sum_{\nu=0}^{\infty} (-1)^\nu a_\nu (\sqrt{3/7}\,\lambda_1\sqrt{\tau+\theta})^{\nu+1} \times B\left[1-(1+[\theta/\tau])^{-7/3};\ \frac{1}{2}, \frac{3\nu+10}{14}\right] \right\} \quad \text{(A-3)}$$

For $(\theta/\tau)<1$, the functions B, ψ and $(\tau+\theta)^{(\nu+1)/2}$ can be expanded into the power series of (θ/τ), as follows:

$$B\left[1-(1+[\theta/\tau])^{-7/3};\frac{1}{2},\frac{3\nu+10}{14}\right] = 2\sqrt{\frac{7\theta}{3\tau}} \times \left\{1-\frac{3\nu+11}{18}\left(\frac{\theta}{\tau}\right) + O\left(\left[\frac{\theta}{\tau}\right]^2\right)\right\} \quad \text{(A-4)}$$

$$\psi(\lambda_1\sqrt{\tau+\theta}) = \psi(\lambda_1\sqrt{\tau}) + \frac{\mathrm{d}\psi(\lambda_1\sqrt{\tau})}{\mathrm{d}\ln\tau}\left(\frac{\theta}{\tau}\right) + O\left(\left[\frac{\theta}{\tau}\right]^2\right) \quad \text{(A-5)}$$

$$(\tau+\theta)^{(\nu+1)/2} = \tau^{(\nu+1)/2}\left\{1+\frac{\nu+1}{2}\left[\frac{\theta}{\tau}\right]+O([\theta/\tau]^2)\right\} \quad \text{(A-6)}$$

Further, from Eq. 16a we obtain the following relation:

$$\frac{\mathrm{d}\psi(\lambda_1\sqrt{\tau})}{\mathrm{d}\ln\tau} = \frac{1}{2}\sum_{\nu=0}^{\infty}(-1)^\nu \nu a_\nu(\sqrt{3/7}\,\lambda_1\sqrt{\tau})^\nu \quad \text{(A-7)}$$

Therefore, taking into account Eqs. A-4—A-7, the integral I_1 can be expanded into the following power series of $\sqrt{\theta/\tau}$:

$$I_1 = \sqrt{\frac{3\pi}{7}} \frac{\sqrt{D_O}C_O^\circ}{1+\exp(\zeta_1)} \left\{ [1-\psi(\lambda_1\sqrt{\tau})] - \frac{2}{\sqrt{\pi}}[(\lambda_1\sqrt{\tau})\phi(\lambda_1\sqrt{\tau})]\sqrt{\theta/\tau} - \left[\frac{\mathrm{d}\psi}{\mathrm{d}\ln\tau}\right](\theta/\tau) + \frac{4}{3\sqrt{\pi}}[(\lambda_1\sqrt{\tau})\phi(\lambda_1\sqrt{\tau})]\left[\frac{1}{6}-\frac{\mathrm{d}\ln\phi}{\mathrm{d}\ln\tau}\right](\theta/\tau)^{3/2} + O([\theta/\tau]^2) \right\} \quad \text{(A-8)}$$

On the other hand, the integral I_2 can be evaluated as follows: Rewriting $\tau+u$ insted of u in Eq. 22 yields

$$I_2 = \frac{1}{\sqrt{\tau}}\int_0^\theta \frac{(i_2/nFq)(1+[u/\tau])^{2/3}\mathrm{d}u}{\sqrt{(1+[\theta/\tau])^{7/3}-(1+[u/\tau])^{7/3}}} = \sqrt{\frac{3}{7}}\int_0^\theta \frac{(i_2/nFq)}{\sqrt{\theta-u}}\left\{1-\frac{1}{3}\left[\frac{\theta-u}{\tau}\right]+O([\theta/\tau]^2)\right\}\mathrm{d}u. \quad \text{(A-9)}$$

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