

GENERAL THEORY OF ALTERNATING CURRENT POLAROGRAPHY FOR ELECTRODE REACTIONS PRECEDED BY SLOW CHEMICAL REACTIONS*

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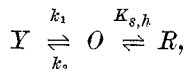
There are many electrode processes in which the electrochemical reaction is coupled with a slow chemical reaction. Such electrode processes constitute an important subject for study.

The theoretical treatment of the kinetics of electrode processes has been based essentially on one of two different standpoints. Gerischer (1951, 1952, 1953*a*, 1953*b*, 1953*c*) and others have argued from considerations of an equivalent circuit. These authors have treated electrode processes with different types of rate-determining steps; and have derived expressions for the equivalent circuit elements.

A second approach is that of Breyer and Hacobian (1954). The latter have based their treatment on the direct measurement of the alternating current. They have presented clear theoretical arguments to show that both the measurement of alternating currents and the interpretation of alternating current against direct voltage curves is simpler and less ambiguous than the impedance measurements and their interpretation in the equivalent circuit method. Breyer, Bauer, and Hacobian (1955), however, have only considered electrode processes with a single rate-determining step.

In the present work, general expressions are developed for the magnitude and the phase of the alternating polarographic current resulting from electrode reactions preceded by a first-order kinetic reaction in solution.

The general reaction considered is :



where the oxidant O is generated by a slow chemical reaction (with rate constants k_1 and k_2) from the substance Y . The reductant R results from the electrode reaction which is characterized by a single, heterogeneous rate constant $K_{s,h}$ following Delahay (1954). The differential equations for the system are set up by applying Fick's laws of diffusion. General solutions for the concentrations of

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oxidant and reductant are then obtained by using the Laplace transformation, and by introducing the appropriate initial and boundary conditions. Finally, the theory of absolute reaction rates is used to obtain general equations for the alternating polarographic current, and for the phase angle introduced by the kinetic reaction.

A ripple voltage superimposed upon a constant voltage is applied across the polarographic cell. As a result, there flows through the cell a current

$$i = i_0 + I \sin \omega t,$$

where i , the instantaneous current flowing through the cell, consists of a direct component i_0 (due to the applied D.C. cathodic polarization) and an alternating component $I \sin \omega t$, the alternating component of the applied voltage is then given by

$$v = V \sin (\omega t + \varphi),$$

where V is the amplitude of the applied ripple and φ is the phase angle between the applied alternating voltage and the resulting alternating polarographic current.

The phase angle φ is then related to the rate constants by equation (1), and the value of the alternating polarographic current I_{peak} at the summit potential E_s , that is, the peak current amplitude, is given by equation (2). In the equations D is the diffusion coefficient assumed to be the same for all the species, t is the time of electrolysis, and ω is the angular frequency of the applied ripple voltage.

$$\tan \varphi = \frac{-(r_1/a + r_4)}{D/K_{s,h} + r_2/a + r_5} \dots \dots \dots (1)$$

$$I_{\text{peak}} = \frac{\frac{n^2 F^2 A D C_0^0}{RT} \left\{ \alpha - \frac{1}{Q} [A] \right\}}{\left(\frac{r_1 + r_4}{a} \right) \frac{1}{V \sin \varphi} + \frac{nF}{RT} \left\{ \frac{\alpha r_3}{a} - (1 - \alpha) r_6 - \frac{1}{Q} [A] \left[\frac{r_3}{a} + r_6 + \frac{V \sin \varphi}{2} (B) - \frac{V \cos \varphi}{2} (C) \right] \right\}} \dots \dots \dots (2)$$

where $a = k_1 + k_2$,

$$r^2 = a^2 + \omega^2,$$

$$A = \frac{\alpha g_1}{a} - (1 - \alpha) g_2,$$

$$B = \frac{\alpha r_1}{a} - (1 - \alpha) r_4,$$

$$C = \frac{\alpha r_2}{a} - (1 - \alpha) r_5,$$

$$Q = \frac{D}{K_{s,h}} + \frac{g_1}{a} + g_2,$$

$$g_1 = 2k_1 \sqrt{\left(\frac{Dt}{\pi}\right)} + k_2 \sqrt{\left(\frac{D}{a}\right)} \operatorname{erf} \sqrt{(at)},$$

$$g_2 = 2 \sqrt{\left(\frac{Dt}{\pi}\right)},$$

$$r_1 = k_1 \sqrt{\left(\frac{D}{2\omega}\right)} + k_2 \sqrt{\left[\frac{D}{2} \left(\frac{r-a}{r^2}\right)\right]},$$

$$r_2 = k_1 \sqrt{\left(\frac{D}{2\omega}\right)} + k_2 \sqrt{\left[\frac{D}{2} \left(\frac{r+a}{r^2}\right)\right]},$$

$$r_3 = \frac{k_1}{\omega} \sqrt{\left(\frac{D}{\pi t}\right)} + k_2 \sqrt{\left(\frac{D}{\pi t}\right)} \left\{ \frac{\omega(1-at)}{r^2} \right\},$$

$$r_4 = r_5 = \sqrt{\left(\frac{D}{2\omega}\right)},$$

$$r_6 = \frac{1}{\omega} \sqrt{\left(\frac{D}{\pi t}\right)}.$$

In the above general theory, when it is assumed that the electrode process consists of a single rate-determining step, the equations for the alternating polarographic current which have been developed by Delahay *et al.* and also by Breyer and co-workers, can be obtained as special cases. This result is obtained, firstly, by making the rate constants for the kinetic reaction very large ($k_1=k_2\rightarrow\infty$), and secondly by setting $\alpha=0.5$. These approximations also make the phase angle ϕ equal to 45° . The latter result for reversible reactions is the same as that obtained by earlier workers.

The details of the derivation will shortly be presented elsewhere. Work is also in progress to apply the theory to particular reaction systems.

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