

# DETERMINATION OF KINETIC PARAMETERS OF ELECTROCHEMICAL REACTIONS BY MEASUREMENT OF FARADAIC DISTORTION\*

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A number of methods have been used in work aimed at the determination of the characteristic kinetic parameters of electron-transfer reactions at electrodes (see, for instance, the review of Delahay<sup>1</sup>). For the study of fast reactions, methods involving alternating voltages or currents of variable frequency, or pulses of voltage, current, or charge, have been applied. The application of these methods is usually limited by the difficulty of separating the faradaic effects of the electrochemical reaction from the non-faradaic effects produced by the electrical double-layer at the surface of the electrode. This difficulty is not encountered when measurements are made of the second-harmonic current in a.c. polarography; an equation is reported here that relates the magnitude of the second-harmonic current to the kinetic parameters characteristic of electron-transfer reactions, permitting calculation of the values of these parameters.

In an earlier communication<sup>2</sup> it had already been pointed out that the measurement of the second harmonic could lead to increased sensitivity in analytical applications; and Delahay, Senda, and Weis<sup>3</sup> commented that the advantage inherent in such a technique could also prove of value in the study of the kinetics of electrode processes.

The derivation of the following equation is based on the same fundamental relations as those used in the theoretical treatment of a.c. polarography (see equation (33) in Chapter 2 of Breyer and Bauer<sup>4</sup> and related discussion). Terms describing the second harmonic are obtained by taking into account those involving  $\cos^2\omega t$ ,  $\sin^2\omega t$ , and  $\cos\omega t \sin\omega t$ , which are ignored in treatments other than that for the redoxokinetic effect (see equations (133) and (152) in Chapter 2 of Breyer and Bauer<sup>4</sup>). The treatment involves no other noteworthy feature, and leads to the expression

$$\Delta i_2 = \frac{n^3 F^3 A C V^2 k \exp P}{2 R^2 T^2 (u_1 W^2 + u_2 W + u_3)} \left( y_1 W^4 + y_2 W^3 + y_3 W^2 + y_4 W + y_5 \right)^{\frac{1}{2}}$$

where

$$u_1 = (\exp P + d^{\frac{1}{2}})^2$$

$$u_2 = 2(\exp P + d^{\frac{1}{2}}) \exp a P$$

$$u_3 = 2 \exp 2a P$$

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<sup>1</sup> Delahay, P., *Advanc. Electrochem. & Electrochemical Engng.*, 1961, **1**, 233.

<sup>2</sup> Bauer, H. H., *J. Electroanal. Chem.*, 1960, **1**, 256.

<sup>3</sup> Delahay, P., Senda, M., and Weis, C. H., *J. Amer. Chem. Soc.*, 1961, **83**, 312.

<sup>4</sup> Breyer, B., and Bauer, H. H., "Alternating Current Polarography and Tensammetry." (John Wiley/Interscience: New York 1963.)

$$y_1 = \frac{1}{4} \frac{(\exp P - d^{\frac{1}{2}})^2}{\exp 2aP}$$

$$y_2 = \frac{(\exp P - d^{\frac{1}{2}})[a \exp P + d^{\frac{1}{2}}(a-1)]}{(\exp P + d^{\frac{1}{2}}) \exp aP}$$

$$y_3 = \frac{2[a \exp P + d^{\frac{1}{2}}(a-1)]^2}{(\exp P + d^{\frac{1}{2}})^2}$$

$$y_4 = \frac{4(a - \frac{1}{2})[a \exp P + d^{\frac{1}{2}}(a-1)] \exp aP}{(\exp P + d^{\frac{1}{2}})^2}$$

$$y_5 = \frac{4(a - \frac{1}{2})^2 \exp 2aP}{(\exp P + d^{\frac{1}{2}})^2}$$

$$P = nF(E - E_0)/RT$$

$$W = k(2/\omega D_R)^{\frac{1}{2}}$$

$$d = D_R/D_O$$

and  $E$  is the direct potential,  $E_0$  the formal standard potential,  $\Delta i_2$  the amplitude of the second-harmonic current,  $A$  the area of the electrode,  $C$  the bulk concentration of

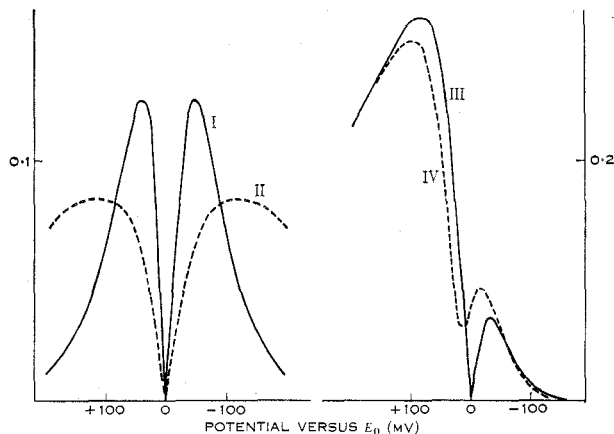


Fig. 1.—Theoretical curves for the second-harmonic current as a function of polarizing potential. The scale of the vertical axis is in units of  $2R^2T^2\Delta i_2/n^3F^3ACV^2k$ . All curves are for  $d = 1$ . Curve I:  $\alpha = 0.5$ ,  $W = 100$ . Curve II:  $\alpha = 0.5$ ,  $W = 0.01$ . Curve III:  $\alpha = 0.1$ ,  $W = 100$ . Curve IV:  $\alpha = 0.1$ ,  $W = 1$ .

the depolarizer,  $V$  the amplitude of the superposed alternating voltage of angular frequency  $\omega$ ,  $k$  the rate constant of the electron-transfer step,  $\alpha$  the transfer coefficient,  $D_O$  and  $D_R$  the diffusion coefficients of the oxidized and reduced species respectively, and  $n$ ,  $F$ ,  $R$ , and  $T$  have their usual significance.

This equation describes curves of the general form shown in Figure 1, having two peaks and a minimum between them. The particular form of the curve is

determined by the values of  $k$ ,  $\alpha$ ,  $\omega$ ,  $D_O$ , and  $D_R$ ; thus, the possibility exists of calculating the kinetic parameters by fitting experimentally obtained curves to the theoretical ones. For this purpose, a considerable number of theoretical curves is required, for various values of the listed parameters; computations are in progress to obtain such a set of curves. Preliminary computations have shown that:

- (1) The magnitudes of  $D_O$  and  $D_R$  affect only the scale of the current and potential axes and this is unlikely to complicate use of the curves to determine kinetic parameters.
- (2) For  $\alpha = 0.5$ , the curve is symmetrical about the minimum; the separation of the peaks increases, and their heights decrease, with increasing frequency.
- (3) For values of  $\alpha$  other than 0.5, the curve is not symmetrical. The ratio of the peak heights, their relation to the minimum current, and the separation of the peaks, as well as the absolute magnitude of the current, are determined by the values of  $\alpha$ ,  $k$ , and  $\omega$ . The exact form of these relations is being computed to provide the criteria for calculations of  $k$  and  $\alpha$ .

At limitingly low frequencies,  $k \gg (2/\omega D_R)^{1/2}$ , the equation takes the particularly simple form

$$\Delta i_2 = \frac{n^3 F^3 A C V^2 k (\exp P - d^{1/2}) \exp(1 - \alpha) P}{4 R^2 T^2 (\exp P + d^{1/2})^2},$$

which shows, *inter alia*, that in this case the second-harmonic current is always zero when  $\exp P = d^{1/2}$ , i.e. at the summit potential of the a.c. wave or the half-step potential of the d.c. polarographic step. Further, differentiation with respect to potential shows that the separation of the peaks is given by

$$\frac{RT}{nF} \ln \frac{3 + (9 - 4\alpha + 4\alpha^2)^{1/2}}{3 - (9 - 4\alpha + 4\alpha^2)^{1/2}}.$$

This corresponds to  $90.5/n$  mV when  $\alpha = 0.5$ , i.e. the same value as the width at half-height of the a.c. wave. However, for other values of  $\alpha$  the separation is greater, showing that even at limiting low frequencies the second-harmonic polarogram is not simply the derivative of the first-harmonic curve, as had been suggested<sup>5</sup> on the basis of earlier<sup>6</sup> equations of general form for a.c. polarography.

<sup>5</sup> Smith, D. E., and Reinmuth, W. H., *Analyt. Chem.*, 1961, **33**, 482.

<sup>6</sup> Tachi, I., and Senda, M., *Bull. Chem. Soc. Japan*, 1955, **28**, 632.