bon gel" formation. Of these two reactions 6 is the more likely. The reaction

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (9)$$

is very fast, competing so successfully with reaction 10

$$R\cdot + R\cdot \longrightarrow RR \qquad (10)$$

that the latter cannot be detected in the presence of oxygen at pressures approaching atmospheric. But on the evidence in this report, reaction 5 occurs to an undetectable extent compared with reaction 10. Although other radical reagents inhibit carbon gel formation, oxygen, which is one of the most efficient radical acceptors in Hevea, does not.[35] This also suggests reaction 6. The occurrence of either (5) or (6) would not explain the formation of carbon radicals capable of continuing the reaction chain as would (7) and (8). Alternative formulations such as (5a) and (6a) may do so

$$R\cdot + C \longrightarrow RC\cdot \qquad (5a)$$

$$RO_2\cdot + C \longrightarrow RO_2C\cdot \qquad (6a)$$

in analogy with, say, addition to an olefinic bond. Studies with graphitized carbon black may help decide between these alternatives.

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Analysis of the Double Pulse Galvanostatic Method for Fast Electrode Reactions

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A rather rigorous analysis is made for the double pulse galvanostatic method for the kinetic study of very fast electrode reactions. An equation is derived for potential–time curves. The ratio of pulse heights is calculated for conditions in which the potential–time curve has a horizontal tangent at the end, t_1, of the first pulse. It is shown that a plot of overvoltage at time t_1 against $t_1^{1/2}$ is linear for curves with a horizontal tangent at t_1. The overvoltage extrapolated at $t_1 = 0$ does not include any concentration polarization component, and the calculation of the exchange current is immediate. Exchange currents for very fast reactions can be seriously in error when concentration polarization is neglected at the end of the first pulse. Theory and experiment are in good agreement for the discharge of mercurous ion on mercury in 0.98 *M* perchloric acid at 25°. Instrumentation is described in detail.

Fast electrode processes are studied by relaxation methods in which either the potential of the electrode being studied or the cell current is changed abruptly or periodically.[3] In galvanostatic methods, a single or a double current pulse is applied to the cell, and potential–time variations are determined. The cell current at any time is the algebraic sum of the faradaic and capacity currents. An analysis of the single pulse method was made by Roitern, Juza and Polujan[4] for electrolysis without concentration polarization and by Berzins and Delahay[5] for processes with concentration polarization. It was found[5] that to minimize concentration polarization the duration of electrolysis must be decreased as the exchange current increases. Even so, very fast electrode reactions cannot be studied by the single-pulse method because an important fraction of the cell current in the initial moments is primarily non-faradaic.[6] This limitation is removed in the double pulse method which was developed by Gerischer and Krause[7] and applied by these authors to the discharge of mercurous ion on mercury. The first pulse, which is of higher amplitude than the second pulse, primarily charges the double layer for the overvoltage required at the current density of the second pulse (Fig. 1). A potential–time curve with a horizontal tangent at time t_1 at the end of the first pulse is obtained when the ratio of pulse heights is properly adjusted (Fig. 2). This ratio is determined by trial and error. Gerischer and Krause assumed that concentration polarization is quite negligible at time t_1, and they readily calculated the exchange current density from the overvoltage at t_1. They realized that their interpretation is approximate, and they determined an order of

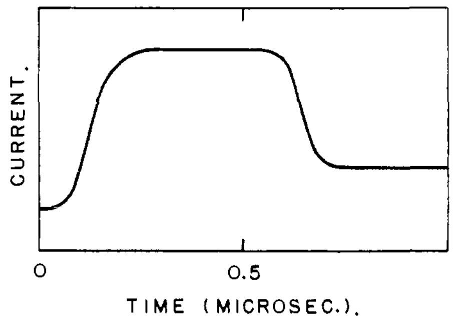

Fig. 1.—Tracing of double pulse. The length of the second pulse was approximately 10 microseconds. See Experimental for discussion of distortion.

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[3] (a) For a review, see for instance P. Delahay, *Ann. Rev. Phys. Chem.*, **8**, 229 (1957); (b) also, P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

[4] W. A. Roitern, W. A. Juza and E. S. Polujan, *Acta Physicochim. U.R.S.S.*, **10**, 389, 845 (1939).

[5] T. Berzins and P. Delahay, THIS JOURNAL, **77**, 6448 (1955).

[6] Gerischer and Krause (ref. 7a) state that the potentialities of the single pulse galvanostatic method are the same as for faradaic impedance measurements because a step function can be expressed by a Fourier series. This does not seem correct, however, because a *steady state* is achieved in faradaic impedance measurements whereas transients are observed in the single pulse method. The limitation is rather the one stated above.

[7] (a) H. Gerischer and M. Krause, *Z. physik. Chem., N.F.*, **10**, 264 (1957); (b) **14**, 184 (1958).

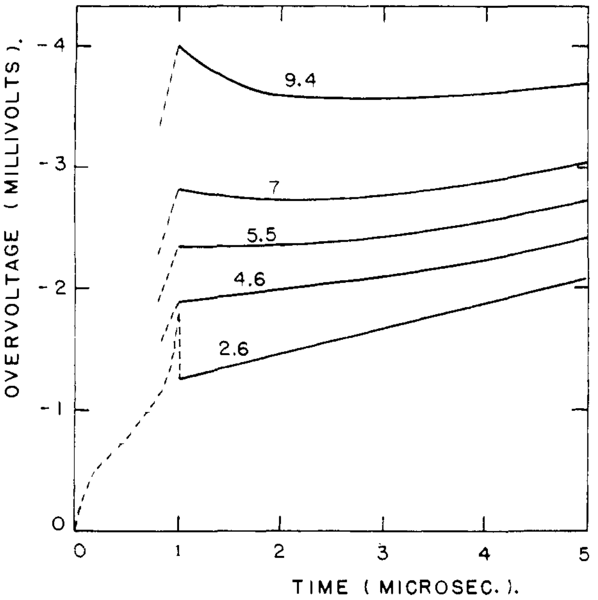

Fig. 2.—Tracings of potential–time curves for the discharge of 0.5 mM mercurous ion on mercury in 0.98 M perchloric acid at 25°. I_2 = 19.0 ma. cm.$^{-2}$, t_1 = 1 microsec. Number on each curve is I_1/I_2. Note third curve with horizontal tangent at t_1. Spurious transient near t_1 (see Experimental) and curves for $t < t_1$ represented only for lower curve.

magnitude of the error. Since the double pulse method has promises for fast reactions, a more rigorous analysis than that of Gerischer and Krause was developed. Its essential results are reported here with a comparison of theory and experiment for the discharge of mercurous ion on mercury. Instrumentation also is described.

Potential–Time Variations

The derivation is the same as for the single-pulse method[5] except that the diffusion problem must now be considered before and after the time t_1 corresponding to the end of the first pulse. The reasoning is as follows.

Consider a reaction O + ne = R, involving only soluble species, in which the rate-determining step and the over-all reaction require n electrons. The total current density, which is constant during each pulse, is set equal to the algebraic sum of the faradaic and non-faradaic components. The faradaic current density is expressed as a function of potential and of the concentrations of O and R at the electrode surface. This function is linearized in terms of the potential—an entirely justified approximation for overvoltages not exceeding a few millivolts. Thus

$$I_f = I_0\left\{\frac{C_O}{C^0_O} - \frac{C_R}{C^0_R} - \frac{nF}{RT}(E - E_e)\right\} \qquad (1)$$

where I_f is the density of the faradaic current; I_0 the exchange current density; the C^0's the bulk concentrations of O and R; the C's the concentrations of these substances at the electrode surface; E the potential in the European convention; E_e the equilibrium potential for C^0_O and C^0_R; and R, T and F have their usual significance. A cathodic current is positive in eq. 1. One has[5]

$$I_0 = nFk_sC^0{}_O{}^{(1-\alpha)}\,C^0{}_R{}^{\alpha} \qquad (2)$$

where α is the transfer coefficient and k_s is the standard rate constant, *i.e.*, the rate constant at the standard potential for the reaction O + ne = R. The parameters I_0 and k_s are formal quantities which depend on the double layer structure. This point will not be taken up since discussions are available.[8]

The non-faradaic current density is simply the product of the differential capacity per unit area by $-\mathrm{d}E/\mathrm{d}t$, the minus sign resulting from the convention that a cathodic current is positive. The resulting expression for the cell current is one of the boundary condition for the diffusion problem. The other boundary condition simply states that the sum of the fluxes for O and R at the electrode surface is equal to zero. Fick's equation for linear diffusion is now solved by Laplace transformation for substances O and R, and the resulting concentrations at the electrode surface are introduced in the current–potential characteristics. Modifications from the derivation previously reported[5] are given in Appendix I.

The potential–time characteristic is for $t > t_1$

$$\begin{aligned} E - E_e = {}& \frac{I_1}{c_1}\frac{1}{\beta - \gamma}\left\{\frac{\gamma}{\beta^2}\left[\exp(\beta^2 t)\,\mathrm{erfc}(\beta t^{1/2}) + 2\beta\left(\frac{t}{\pi}\right)^{1/2} - 1\right] - \frac{\beta}{\gamma^2}\left[\exp(\gamma^2 t)\mathrm{erfc}(\gamma t^{1/2}) + 2\gamma\left(\frac{t}{\pi}\right)^{1/2} - 1\right]\right\} \\ & - \frac{I_1 - I_2}{c_1}\frac{1}{\beta - \gamma}\left\{\frac{\gamma}{\beta^2}\left\{\exp[\beta^2(t - t_1)]\mathrm{erfc}[\beta(t - t_1)^{1/2}] + 2\beta\left(\frac{t - t_1}{\pi}\right)^{1/2} - 1\right\} - \frac{\beta}{\gamma^2}\left\{\exp[\gamma^2(t - t_1)]\mathrm{erfc}[\gamma(t - t_1)^{1/2}] + 2\gamma\left(\frac{t - t_1}{\pi}\right)^{1/2} - 1\right\}\right\} \end{aligned} \qquad (3)$$

with

$$\beta = \frac{I_0}{2nF}\left(\frac{1}{D^{1/2}{}_OC^0{}_O} + \frac{1}{D^{1/2}{}_RC^0{}_R}\right) + \left[\frac{I_0{}^2}{4n^2F^2}\left(\frac{1}{D^{1/2}{}_OC^0{}_O} + \frac{1}{D^{1/2}{}_RC^0{}_R}\right)^2 - \frac{nF}{RT}\frac{I_0}{c_1}\right]^{1/2} \qquad (4)$$

and γ being given by the same equation as 4 except for a minus sign in front of the quantity between brackets.[9] Equation 3 in which the term in $I_1 - I_2$ is dropped also holds for $0 < t < t_1$. The equation for $0 < t < t_1$ is the same as the one previously derived (see eq. 18 of ref. 5). New notations are: I_1 and I_2 the current densities during the first and second pulses, respectively; c_l the differential capacity of the double layer per unit area (c_1 is assumed to be constant over the interval, $E - E_e$, of a few millivolts); t the time as counted from the beginning of the first pulse.

Determination of Exchange Current Density Potential with Horizontal Tangent at Time t_1.—One can show (Appendix I) that the potential–time curve for sufficiently small values of t_1 has a horizontal tangent at t_1 at a potential E_h such that

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(8) See for instance M. Breiter, M. Kleinerman and P. Delahay, This Journal, **80**, 5111 (1958). A detailed bibliography is given.

(9) Note a misprint in the value of β in eq. 19 of ref. 5 and that a minus sign should precede the second member of eq. 18.

$$E_{\mathrm{h}} - E_{\mathrm{e}} = \frac{RT}{nF}\frac{I_2}{I_0}\left\{\begin{aligned}&1 + \frac{4}{3\pi^{1/2}}\frac{I_0}{nF}\left(\frac{1}{D^{1/2}{}_{\mathrm{O}}C^0{}_{\mathrm{O}}} + \frac{1}{D^{1/2}{}_{\mathrm{R}}C^0{}_{\mathrm{R}}}\right)t_1^{1/2}\\ &+\left(1 - \frac{9\pi}{32}\right)\left[\frac{4}{3\pi^{1/2}}\frac{J_0}{nF}\left(\frac{1}{D^{1/2}{}_{\mathrm{O}}C^0{}_{\mathrm{O}}} + \frac{1}{D^{1/2}{}_{\mathrm{R}}C^0{}_{\mathrm{R}}}\right)\right]^2 t_1 + \ldots\end{aligned}\right\} \quad (5)$$

It follows from eq. 5 that, for sufficiently small values of t_1, *a plot of* $E_{\mathrm{h}} - E_{\mathrm{e}}$ *against* $t_1^{1/2}$ *yields a straight line whose intercept at* $t_1 = 0$ *is* $-(RT/nF)\cdot(I_2/I_0)$, *i.e., the overvoltage for* I_2 *without concentration polarization (eq. 1)*. This provides a very simple experimental method for the determination of the exchange current density I_0 (Fig. 3). The slope of the $E_{\mathrm{h}} - E_{\mathrm{e}}$ against $t_1^{1/2}$ line is proportional to I_2 and inversely proportional to $[(1/D^{1/2}{}_{\mathrm{O}}C^0{}_{\mathrm{O}} + (1/D^{1/2}{}_{\mathrm{R}}C^0{}_{\mathrm{R}})]$. These properties are verified experimentally (Fig. 3 and Table I). The intercept at $t_1 = 0$ depends of course on the C^0's since I_0 varies with the concentrations. The values of slope × $(C^0{}_{\mathrm{Hg_2^{++}}}/I_2)$ in Table I are in good agreement with the theoretical value −0.0166 (units of Table I) calculated from eq. 5 and the diffusion coefficient $D_{\mathrm{Hg_2^{++}}} = 0.91 \times 10^{-5}$ cm.$^{-2}$ sec.$^{-1}$ deduced from polarographic data.[10]

TABLE I

SLOPE OF THE $E_{\mathrm{h}} - E_{\mathrm{e}}$ AGAINST $t_1^{1/2}$ PLOT FOR MERCUROUS ION DISCHARGE[a] AT 25°

$C^0{}_{\mathrm{Hg2^{++}}}$, m$M$ l.$^{-1}$	I_2, ma. cm.$^{-2}$	Slope, v. sec.$^{-1/2}$	Slope × $(C^0{}_{\mathrm{Hg2^{++}}}/I_2)$	I_0, ma. cm.$^{-2}$
0.25	19	−1.34	−0.0176[b]	89
0.5	19	−0.68	− .0179	144
1	19	− .34	− .0179	248
1	38	− .79	− .0208	257
2	38	− .32	− .0169	415
		Av.	− .0182	

[a] Data from Fig. 3. [b] Units of this table.

It is seen from Fig. 3 that *a serious error on the exchange current may result when concentration polarization is neglected at* t_1. Thus, for the 1 mM solution one has I_0 = 248 ma.cm.$^{-2}$ (Table I) whereas I_0 calculated from the overvoltage at t_1 = 1 microsec. is 180 ma.cm.$^{-2}$ The error would be larger for $t_1 > 1$ microsec. Gerischer and Krause[7] reported for t_1 = 1.5 microsec. and the same solution and temperature I_0 = 125 to 140 ma.sec.$^{-1}$ without correction for concentration polarization.

The transfer coefficient α is determined, as in other relaxation methods, from the variations of I_0 with one of the C_0, the other C_0 being kept constant. The linear plot of log I_0 against the logarithm of the varying concentration readily yields α (eq. 2). Excellent linearity was obtained for the data of Table I, and the value $\alpha = 0.24$ was deduced (*versus* $\alpha = 0.30 \pm 0.03$ according to Gerischer and Krause[7]).

The plot of $E_{\mathrm{h}} - E_{\mathrm{e}}$ for large t_1's, as shown in Appendix I, is also linear, but the slope is now $^3/_2$ of the slope for small values of t_1 and the intercept is

$$-\frac{RT}{nF}\frac{I_2}{I_0}\left[1 - \left(1 - \frac{2}{\pi}\right)\frac{RT}{n^3F^3}\left(\frac{1}{D^{1/2}{}_{\mathrm{O}}C^0{}_{\mathrm{O}}} + \frac{1}{D^{1/2}{}_{\mathrm{R}}C^0{}_{\mathrm{R}}}\right)^2 I_0\, c_1\right]$$

The variations of $E_{\mathrm{h}} - E_{\mathrm{e}}$ against $t_1^{1/2}$ are thus represented by an upward curve which, for extreme values of t_1, can be identified with two straight lines whose slopes are in the ratio 2:3 (slope for small t_1's to slope for large t_1's). The condition that $E_{\mathrm{h}} - E_{\mathrm{e}}$ do not exceed a few millivolts must be satisfied, and the extrapolation for large t_1's may well not be applied when experimental overvoltages exceed the above permissible value. The extrapolation for small t_1's is used in practice, and the dependence of the intercept at $t_1 = 0$ on $C^0{}_{\mathrm{O}}$ and/or $C^0{}_{\mathrm{R}}$ supplies the necessary verification that the extrapolation for small t_1's does hold.

Evaluation of the Ratio I₂/I₁.—The correct value of I_2/I_1 for which a horizontal tangent is observed at t_1 is given by eq. 13 in Appendix I. A simpler expression can be obtained on the assumption that there is no concentration polarization for $t \ll t_1$. Thus, the absolute value of the change in the double layer charge per unit area for the variation of potential $E_{\mathrm{h}} - E_{\mathrm{e}}$ is $|c_1\,(E_{\mathrm{h}} - E_{\mathrm{e}}|)$, *i.e.*, $c_l(RT/nF)(I_2/I_0)$. This change in charge is also I_1t_1 for charging at constant current density. Hence

$$\frac{I_2}{I_1} = \frac{1}{c_1}\frac{nF}{RT}I_0\,t_1 \quad (6)$$

This is only a *very approximate* value because of the assumption that there is no concentration polarization. One obviously must have $I_2/I_1 < 1$ since, otherwise, there would be no point in the use of the double pulse method.

One can show (Appendix I) that eq. 6 holds provided that

$$\frac{1}{nF}\left(\frac{1}{D^{1/2}{}_{\mathrm{O}}C^0{}_{\mathrm{O}}} + \frac{1}{D^{1/2}{}_{\mathrm{R}}C^0{}_{\mathrm{R}}}\right)I_0t_1^{1/2} \ll 1 \quad (7)$$

and

$$\frac{nF}{RT}\frac{1}{c_1}I_0t_1 \ll 1 \quad (8)$$

Condition 8 is also obtained by expanding the exponentials and error functions in eq. 3 (as written for $t < t_1$). It is then concluded that the potential varies linearly with time (charging of a capacitor at constant current) provided that condition 8 is fulfilled (see Appendix).

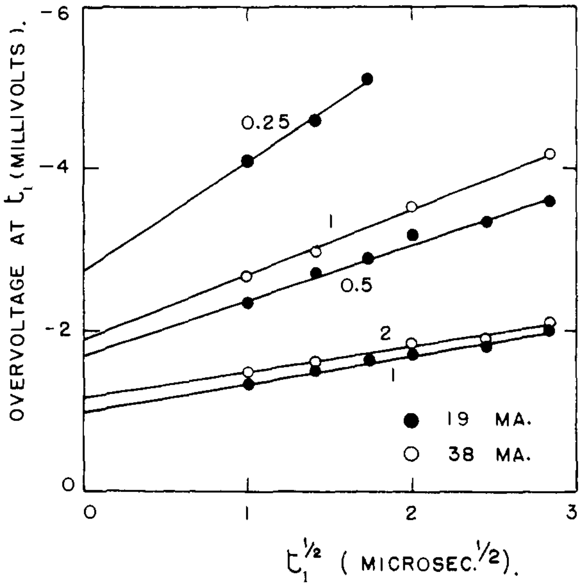

Fig. 3.—Plot of the overvoltage $E_{\mathrm{h}} - E_{\mathrm{e}}$ against t_1 for the discharge of mercurous ion in 0.98 M perchloric acid. Numbers on lines are the concentration of mercurous in millimoles per liter. I_2 = 19 and 38 ma. cm.$^{-2}$.

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[10] L. Meites, "Polarographic Techniques," Interscience Publishers. Inc., New York, N. Y., 1955, p. 272. $D_{\mathrm{Hg_2^{++}}}$ was computed from the diffusion current constant for Hg(I) in 0.1 M HNO₃.

In practice, conditions 7 and 8 are hardly satisfied for very fast reactions and eq. 6 gives at best an order of magnitude of I_2/I_1. For instance, for the 1 mM mercurous solution (Table I) and $t_1 = 1$ microsec. the quantity in the first member of eq. 7 is approximately 4 ($D_0 = 0.91 \times 10^{-5}$ cm.^{2} sec.$^{-1}$), and condition 7 is not fulfilled at all. Likewise, the quantity in eq. 8 for the same data is approximately 0.5. Equation 13 in Appendix I can be applied to the calculation of I_2/I_1 but, in general, I_2/I_1 is determined by trial and error.

Experimental

Instrument.—The double pulse generator was composed of two single pulse generators (Tektronix, model 163) which were triggered manually with another pulse generator (Tektronix, model 162). The two pulses were mixed in a twin-triode circuit with common cathode. The bridge circuit for compensation of the ohmic drop in the cell was similar to the one previously used for single pulse studies.[5] It was inserted in the cathode circuit of the mixer.

Pulse heights were adjusted by variation of the grid voltages of the mixer with separate battery supplies. Two precautions were observed: (a) the plate current was in the linear segment of the tube characteristic; and (b) the grid voltage supplies were of low resistance, *e.g.*, 200 ohm potentiometer in series with a 500 ohm resistance connected to a 22.5 volt battery. The rise and cut-off times increased markedly when these precautions were not taken. Further adjustment of pulse heights was made by variation of the plate voltages of the mixer (separate supplies). The pulse height ratio varied from 2 to 12 in this study, but much larger ratios could have been obtained. The low residual plate current through the bridge in the absence of pulse generation was compensated with a potentiometer.

The rise and cut-off time was approximately 0.2 microsec. for any pulse length (Fig. 1). The pulse generators that were used had approximately a 0.2 microsec. rise and cut-off time, and distortion thus resulted from the pulse generators rather than the mixer. Pulse generators with a rise time of 0.02 microsec. (Hewlett–Packard, model 212A) became available to us after completion of this study.

Rise times of the preamplifiers, as given by the manufacturer, were as follows: PA, less than 0.03 microsec.; 53/54G "Tektronix," 0.035 microsec. The combination of these preamplifiers, at maximum gain, had a linear response for input voltages up to 80 millivolts. The input voltage did not exceed 50 millivolts in this study (cell resistance of approximately 5.0 ohms). The maximum sensitivity was 0.5 millivolt per centimeter deflection.

Even with good electronic design, spurious short transients (perhaps 0.1 microsec. or less) were observed on potential–time curves very near time t_1 (Fig. 2, transient shown only for the lower curve). Photography of potential–time curves for $t < t_1$ was difficult even with Kodak Triple X film because of the high writing speed. (Prefogging was not used.) These transients were due, it is believed, to asymmetry in the circuit and to the finite time constant of the connecting shielded cables, etc. These transients did not interfere with the measurements.

Cell.—A cell with hanging mercury drop similar to the one previously described[5] was utilized. A dropping mercury electrode could not be used because ohmic drop compensation is difficult in fast recordings with an electrode of continuously varying area.

Solution.—Solutions were prepared from analytical grade reagents and bidistilled water (over potassium permanganate). The concentration of perchloric acid was determined by titration. The solution was freed of oxygen by the bubbling of nitrogen. This gas was passed over charcoal in Dry Ice to remove traces of oil. Adsorption of neutral impurities was minimized because of the markedly anodic potential of the mercury drop.

Conclusion

Application of the double pulse galvanostatic method to very fast electrode processes appears promising for two reasons: (1) correction for concentration polarization is simple; and (2) instrumentation is relatively not too complicated. However, kinetic parameters can be seriously in error when correction for concentration polarization is not made.

The method is definitely superior to the single pulse method in the study of very fast reactions. However, the latter method has the advantage of simplicity (with impedance measurements and the potentiostatic method), and application of the double pulse method is hardly justified in the study of moderately fast electrode reactions. Comparison of the potentialities of the double pulse method with the faradaic rectification method recently developed by Barker and co-workers[11] should be of interest.

It is to be noted that an ideal galvanostatic method with constant faradaic current easily can be conceived (Appendix II). Theory is very simple but instrumentation would be more complicated than for the double pulse method.

Acknowledgment.—This investigation was supported by the Office of Naval Research.

Appendix I

Derivation of Equation 3.—Equation 35 of ref. 5 for the single pulse method is now replaced by

$$\bar{E}(s) = -\frac{I_1}{c_1}\frac{s^{1/2}+a}{s^{3/2}(s+as^{1/2}+b)} + \frac{I_1-I_2}{c_1}\frac{s^{1/2}+a}{s^{3/2}(s+as^{1/2}+b)}e^{-st_1} \quad (9)$$

with

$$a = \frac{I_0}{nF}\left(\frac{1}{D^{1/2}{}_{\mathrm{O}}C^0{}_{\mathrm{O}}} + \frac{1}{D^{1/2}{}_{\mathrm{R}}C^0{}_{\mathrm{R}}}\right) \quad (10)$$

$$b = \frac{nF}{RT}\frac{I_0}{c_1} \quad (11)$$

By factorization of the denominator in eq. 9 there follows

$$\bar{E}(s) = \frac{I_1}{c_1}\frac{1}{\beta-\gamma}\left[\frac{1-(a/\beta)}{s(s^{1/2}+\beta)} - \frac{1-(a/\gamma)}{s(s^{1/2}+\gamma)} + \frac{(a/\beta)-(a/\gamma)}{s^{3/2}}\right] \quad (12)$$

$$-\frac{I_1-I_2}{c_1}\frac{1}{\beta-\gamma}\left[\frac{1-(a/\beta)}{s(s^{1/2}+\beta)}e^{-st_1} - \frac{1-(a/\gamma)}{s(s^{1/2}+\gamma)}e^{-st_1} + \frac{(a/\beta)-(a/\gamma)}{s^{3/2}}e^{-st_1}\right]$$

where β and γ are defined by eq. 4.

By noting the following transforms one obtains eq. 3 for the potential–time curve from eq. 12

$$L^{-1}\frac{1}{s(s^{1/2}+l)} = \frac{1}{l}[1-\exp(l^2t)\mathrm{erfc}(lt^{1/2})]$$

$$L^{-1}\frac{1}{s^{3/2}} = 2\left(\frac{t}{\pi}\right)^{1/2}$$

$$L^{-1}\frac{\exp(-st_1)}{s(s^{1/2}+l)} = \begin{cases} 0 & (0 < t < t_1) \\ \frac{1}{l}\{(1-\exp[l^2(t-t_1)]\mathrm{erfc}[l(t-t_1)^{1/2}]\} & (t > t_1) \end{cases}$$

$$L^{-1}\frac{\exp(-st_1)}{s^{3/2}} = \begin{cases} 0 & (0 < t < t_1) \\ 2\left(\frac{t-t_1}{\pi}\right)^{1/2} & (t > t_1) \end{cases}$$

Potential with Horizontal Tangent at Time t_1.—By prescribing from eq. 3 that $\mathrm{d}(E - E_e)/\mathrm{d}t = 0$ at t_1 one obtains the condition for a horizontal tangent at t_1

$$\frac{I_2}{I_1} = 1 + \frac{1}{\beta-\gamma}[\gamma\exp(\beta^2t_1)\mathrm{erfc}(\beta t_1{}^{1/2}) - \beta\exp(\gamma^2t_1)\mathrm{erfc}(\gamma t_1{}^{1/2})] \quad (13)$$

By introduction of this value of I_2/I_1 in eq. 3 there follows

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[11] G. C. Barker, *Anal. Chim. Acta*, **18**, 118 (1958); (b) G. C. Barker, R. L. Faircloth and J. A. W. Gardner, *Nature*, **181**, 247 (1958).

$$E_h - E_e = \frac{I_2}{c_1} \frac{\frac{\gamma}{\beta^2}\left[\exp(\beta^2 t_1)\operatorname{erfc}(\beta t_1^{1/2}) + 2\beta\left(\frac{t_1}{\pi}\right)^{1/2} - 1\right] - \frac{\beta}{\gamma^2}\left[\exp(\gamma^2 t_1)\operatorname{erfc}(\gamma t_1^{1/2}) + 2\gamma\left(\frac{t}{\pi}\right)^{1/2} - 1\right]}{\gamma[\exp(\beta^2 t_1)\operatorname{erfc}(\beta t_1^{1/2}) - 1] - \beta[\exp(\gamma^2 t_1)\operatorname{erfc}(\gamma t_1^{1/2}) - 1]} \quad (14)$$

Equation 5 is obtained for small t_1 by expansion in series of the exponentials and error functions. For large t_1's one obtains by the same procedure

$$E_h - E_e = -\frac{RT}{nF}\frac{I_2}{I_0}\left\{\begin{aligned} &1 - \left(1 - \frac{2}{\pi}\right)\frac{RT}{nF}\left[\frac{I_0}{nF}\left(\frac{1}{D^{1/2}{}_O C^0{}_O} + \frac{1}{D^{1/2}{}_R C^0{}_R}\right)\right]^2 \frac{c_1}{I_0} \\ &+ \frac{2}{\pi^{1/2}}\frac{I_0}{nF}\left(\frac{1}{D^{1/2}{}_O C^0{}_O} + \frac{1}{D^{1/2}{}_R C^0{}_R}\right) t_1^{1/2} \\ &- \frac{1}{\pi^{1/2}}\frac{RT}{nF}\frac{I_0}{nF}\left(\frac{1}{D^{1/2}{}_O C^0{}_O} + \frac{1}{D^{1/2}{}_R C^0{}_R}\right)\frac{c_1}{I_0}\frac{1}{t_1^{1/2}} \dots \end{aligned}\right\} \quad (15)$$

Derivation of Conditions 7 and 8.—By expanding eq. 14 in a convergent series one has

$$E_h - E_e = -\frac{I_2}{c_1}\frac{1}{\beta\gamma}\left[1 - (\beta + \gamma)\frac{f(\beta t_1^{1/2}) - f(\gamma t_1^{1/2})}{\beta f(\beta t_1^{1/2}) - \gamma f(\gamma t_1^{1/2})}\right] \quad (16)$$

where

$$f(y) = 1 - \frac{4}{3\pi^{1/2}}y + \frac{1}{2}y^2 - \frac{8}{15\pi^{1/2}}y^3 + \frac{1}{6}y^4 \dots \quad (17)$$

By introducing in eq. 16 β and γ from eq. 4 there follows

$$E_h - E_e = -\frac{RT}{nF}\frac{I_2}{I_0}\left[1 + \frac{4}{3\pi^{1/2}}pI_0 \frac{1 - \left(\frac{3\pi^{1/2}}{8}p + \frac{2}{5}q\right)I_0 + \left(\frac{2}{5}p^2 + \frac{\pi^{1/2}}{4}pq + \frac{51}{140}q^2\right)I_0^2 \dots}{1 - \left(\frac{4}{3\pi^{1/2}}p + \frac{1}{2}q\right)I_0 + \left(\frac{1}{2}p^2 + \frac{16}{15\pi^{1/2}}pq + \frac{1}{6}q^2\right)I_0^2 \dots}\right] \quad (18)$$

where

$$p = \frac{1}{nF}\left(\frac{1}{D^{1/2}{}_O C^0{}_O} + \frac{1}{D^{1/2}{}_R C^0{}_R}\right) t_1^{1/2} \quad (19)$$

$$q = \frac{nF}{RT}\frac{1}{c_1}t_1 \quad (20)$$

Hence, conditions 7 and 8 are obtained.

Derivation of Condition 8 and Variations of Potential for $t < t_1$.—One has

$$E - E_e = -\frac{I_1}{c_1}\left\{\begin{aligned} &t - \beta\gamma t^2\left[\frac{1}{2} - \frac{8}{15\pi^{1/2}}(\beta + \gamma)t^{1/2} + \frac{1}{6}(\beta^2 + \beta\gamma + \gamma^2)t\right. \\ &\left. - \left(\frac{16}{105\pi^{1/2}}\right)(\beta + \gamma)(\beta^2 + \gamma^2)t^{3/2} + \dots\right] \end{aligned}\right\} \quad (21)$$

or, after substitution of β and γ from eq. 4

$$E - E_e = -\frac{I_1}{c_1}\left\{\begin{aligned} &t - \frac{nF}{RT}\frac{I_0}{c_1}t^2\left\{\frac{1}{2} - \frac{8}{15\pi^{1/2}}\frac{I_0}{nF}\left(\frac{1}{D^{1/2}{}_O C^0{}_O} + \frac{1}{D^{1/2}{}_R C^0{}_R}\right)t^{1/2}\right. \\ &\left.+ \frac{1}{6}\left[\left(\frac{I_0}{nF}\right)^2\left(\frac{1}{D^{1/2}{}_O C^0{}_O} + \frac{1}{D^{1/2}{}_R C^0{}_R}\right)^2 - \frac{nF}{RT}\frac{I_0}{c_1}\right]t \dots\right\} \end{aligned}\right\} \quad (22)$$

Hence, one has the condition $I_0 t_1 \ll 2(RT/nF)c_1$ which is the same as condition 8 except for the factor 2.

Appendix II

Galvanostatic Method with Constant Faradaic Current.—If $c_1 = 0$ one has[5,12] for a constant faradaic current density I_f and for a time much shorter than the transition time

$$E - E_e = -\frac{RT}{nF}I_f\left[\frac{1}{I_0} + \frac{2}{\pi^{1/2}nF}\left(\frac{1}{C^0{}_O D^{1/2}{}_O} + \frac{1}{C^0_R D^{1/2}{}_R}\right)t^{1/2}\right] \quad (23)$$

or

$$E - E_e = -(A + Bt^{1/2}) \quad (24)$$

where A and B are constants independent of time. The change in the double layer charge is $|Q| = |c_1(E - E_e)|$, *e.g.*, $|Q| = c_1(A + Bt^{1/2})$. The capacity current density $I_c = dQ/dt$, is

$$I_c = \frac{1}{2}c_1 B t^{-1/2} \quad (25)$$

The current pulse for a galvanostatic electrolysis at constant faradaic current density should be of the form

$$I_f + \frac{1}{2}c_1 B t^{-1/2}$$

However, generation of rectangular double pulses is simpler.

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[12] T. Berzins and P. Delahay, *J. Chem. Phys.*, **23**, 972 (1955; *Z. Elektrochem.*, **59**, 792 (1955).