Cyclic Chronopotentiometry

Diffusion Controlled Electrode Reaction of a Single Component System

HARVEY B. HERMAN and ALLEN J. BARD

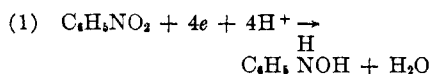*Department of Chemistry, The University of Texas, Austin, Texas*

▶ An electroanalytical method for studying electrode reactions, called cyclic chronopotentiometry, in which the applied current is successively reversed at each transition, is proposed. A circuit for carrying out automatic current reversals is described. The equations for the successive transition times for linear diffusion in a single component system have been derived and solved, and the theoretical results have been confirmed experimentally.

CYCLIC VOLTAMMETRY (CV) is a useful technique for studying electrode reactions (4). By repeatedly reversing the direction of a potential sweep and observing the current, electrode reactions of both the original electroactive substance, and various electroactive intermediates and products, can be studied. Unfortunately a quantitative description of this method is not available; the prevailing mass transfer conditions at the electrode are sufficiently complex that an equation for even the first potential sweep cannot be written in closed form, and the task of obtaining quantitative relations for the subsequent sweeps seems very difficult. We pro-
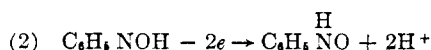
pose a method, cyclic chronopotentiometry (CC), in which a constant current is alternately reversed at potentials taken at the transition times of the various waves. The information obtainable by this technique is similar to that of cyclic voltammetry, but the mathematical treatment is simpler, primarily because the total flux at the electrode surface at any time is constant and known. Application of some recently discussed techniques of the mathematical treatment of chronopotentiometry (5, 8) allows a relatively simple solution of the equations of interest.

A cyclic chronopotentiogram for the nitrobenzene system is shown in Figure 1. The corresponding CV of nitrobenzene, under slightly different conditions, has also been described (6). The reduction of nitrobenzene in acidic, aqueous solutions has been shown to occur by the following mechanism (6, 8):
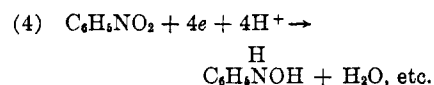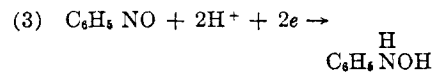
First (reduction) scan:

(1) $C_6H_5NO_2 + 4e + 4H^+ \rightarrow$
$$C_6H_5NOH + H_2O$$

First reversal (oxidation) scan:

(2) $C_6H_5NOH - 2e \rightarrow C_6H_5NO + 2H^+$

Second reversal (reduction) scan:

(3) $C_6H_5NO + 2H^+ + 2e \rightarrow$
$$C_6H_5NOH$$

(4) $C_6H_5NO_2 + 4e + 4H^+ \rightarrow$
$$C_6H_5NOH + H_2O, \text{ etc.}$$

The usefulness of repeated reversals, as opposed to a single reversal (8), is evident. As in CV, the curves are easily compared with one another, and the appearance of new intermediates—e.g., nitrosobenzene—is readily observed. However, these curves are amenable to quantitative treatment, even when complicating chemical reactions occur.

The present paper will be concerned with the instrumentation for CC and with the theoretical treatment of a single oxidation-reduction system, with no kinetic complications. Subsequent communications will describe more complex systems.

EXPERIMENTAL

The basic chronopotentiometric instrumentation and cells were of a conventional design. Mercury pool and platinum electrodes, both shielded for linear diffusion, were used. The solutions, at room temperature, (23° ± 1° C.), were deaerated for at least 15 minutes with prepurified nitrogen.

Although the current can be reversed manually at the proper potentials, the reproducibility of reversal is improved by using a trigger circuit which automatically reverses the current when the potential reaches preset cathodic and anodic limits. The relatively simple circuit used to perform this reversal shown in Figure 2 is based on a triode amplifier and relay. The success of the circuit depends upon the fact that the current needed to throw a sensitive relay is reproducible and that the drift in the triode characteristics is so small that elaborate stabilization measures are unnecessary. Basically, the circuit is similar to the one used to reverse a motor in CV when a microswitch is contacted and released (1); in this case the tubes and relays act as the microswitches.

The operation of this circuit is as follows. Initially the relays are in the positions shown in Figure 2. $V 1$ is
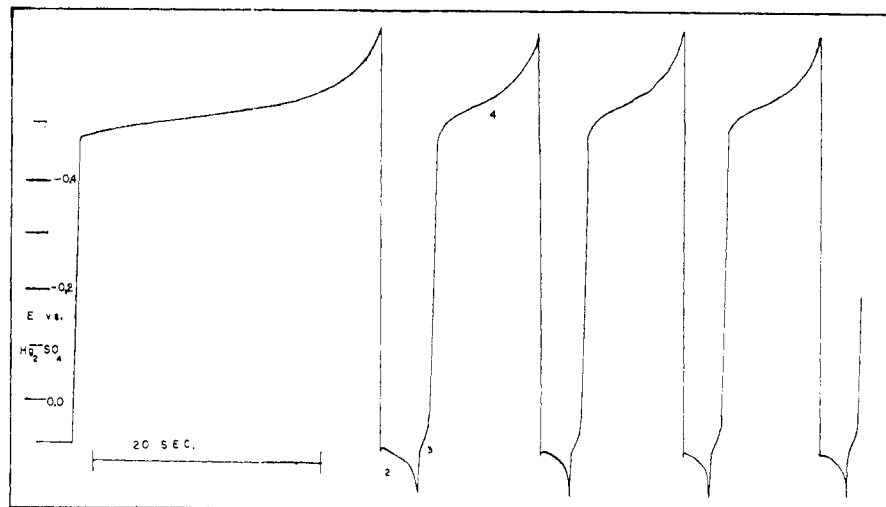

Figure 1. Cyclic chronopotentiogram of nitrobenzene

Solution contained 0.5M KHSO$_4$, 1.5M H$_2$SO$_4$, and 2.5mM nitrobenzene. Current density was 0.370 ma. per sq. cm.

biased such that as the working electrode potential becomes negative (with respect to the reference electrode) the grid of V 1 becomes more positive, causing the current in the coil of RL 1 to increase. At the preset cathodic limit potential the current becomes large enough to cause RL 1 to close, causing RL 2, RL 3, and RL 4, to close and latch. RL 3 reverses the current, and RL 2 shorts the coil of RL 1, causing it to reopen. The action of RL 1 is then momentary (acting as a microswitch). V 2 is biased such that when the working electrode becomes more positive (with respect to the reference electrode) the grid of V 2 (normally conducting) becomes more negative, decreasing the current in the coil of RL 5. When the potential reaches the preset anodic limit, the current in RL 5 decreases enough to allow RL 5 to release, unlatching RL 2, RL 3, and RL 4. The electrolysis current again reverses; RL 4 shorts the 2.7-K. resistor in the plate circuit of V 2, causing the plate current to increase, and allowing RL 5 to close again, setting the circuit back to its initial conditions, in anticipation for the next reversal. The action of RL 5 is also momentary. The rather involved shorting procedure is necessary because of hysteresis in the relay action; that is the relays close and release at different coil currents. RL 1 and RL 5 contain auxiliary poles (not shown) that can be used to activate circuits for automatic measurement of transition times.

This circuit has the advantage of being inexpensive and stable and can be used to measure transition times where the potential is varying rapidly; the switching time is about 30 mseconds. The switching potentials, stable to within ±10 mv., were set before each series of trials with a potentiometer. The shorting double-pole, double-throw switch in the input shorts the input of the triodes when the leads are disconnected, and tends to make the circuit more stable.

THEORETICAL

Cyclic chronopotentiometry is a special case of chronopotentiometry with programmed step current impulses, which has been treated theoretically by several authors. Testa and Reinmuth (8) solved Fick's law equations, using the Laplace transform, to obtain a general solution for step current impulses, and gave experimental results for a single current reversal (with a change in current magnitude possible). Murray and Reilley (5) introduced the "response function additivity" principle, which greatly simplifies the mathematical treatment of new chronopotentiometric problems, especially those involving multicomponent systems and current variations. The equation for calculating the transition times for a multicomponent system for an arbitrary current program is [(5) Equation 63].
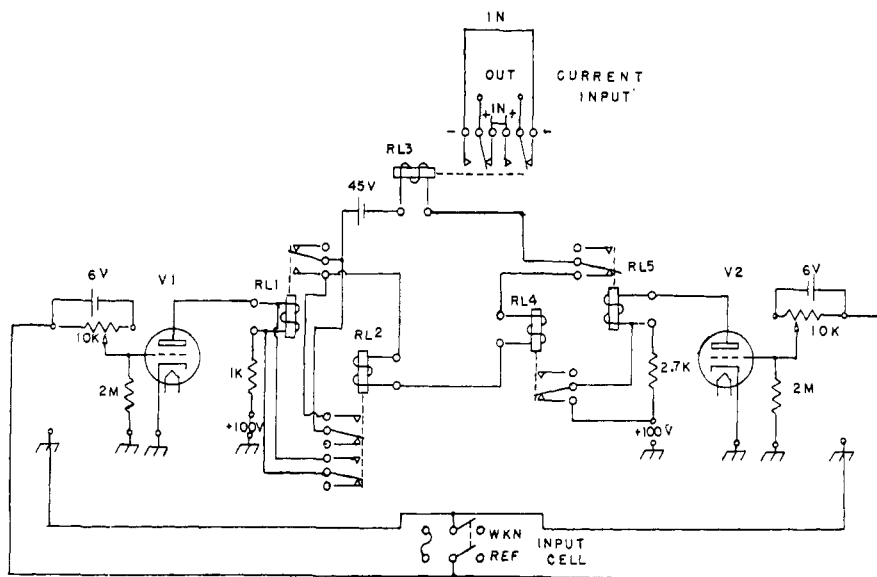
Figure 2. Schematic diagram for automatic current reversing circuit

V 1, V 2, 12AU7A; RL 1, RL 2, RL 3, RL 4, RL 5, Sensitive d.c. relays, 6.3 ma., R405-2-AS-2K(1), Iron Fireman Mfg. Co., Portland, Ore.

$$\sum_m n_m F D_m^{1/2}[C^\circ_m - C_m(0, t)] =$$

$$\sum_p Z_p (0, t - t_p) \quad (1)$$

where C°_m is the initial concentration of the mth species, and $C_m (0, t)$ is its concentration at the electrode surface at time t, $Z_p(0, t-t_p)$ is the current impulse response function, and the other symbols have their usual meanings. Murray and Reilley presented this equation by an essentially intuitive and empirical approach. Since this valuable relation will be used in this and subsequent communications, we have rederived this equation rigorously (Appendix I).

We consider here the case where only a single oxidation-reduction system

$$O + ne \rightleftarrows R \quad (2)$$
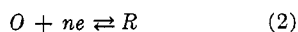
is present, with initial concentrations of C°_O and C°_R, respectively. Semi-infinite linear diffusion and constant current densities, i_{Red} and i_{Ox} are assumed. Although the following treatment is given for an initial reduction, followed by reversals of current, the final results apply equally well to an initial oxidation. At the first transition time, τ_1 and all successive odd-numbered transitions (reductions), the concentration of O at the electrode surface, $C_o (0,\tau)$, is zero, and Equation 1 becomes:

$$C^\circ_O = \frac{2i_{Red}}{nF(D_O\pi)^{1/2}} [(\tau_1 + \tau_2 + \ldots \tau_n)^{1/2} - R(\tau_2 + \ldots \tau_n)^{1/2} + \ldots R(\tau_n)^{1/2}] \quad (3)$$

where

$$R = \frac{i_{Ox} + i_{Red}}{i_{Red}} \quad (4)$$

For all even-numbered transitions (oxidations),

$C_R (0, \tau)$ is zero, and

$$C^\circ_R = \frac{-2i_{Red}}{nF(D_R\pi)^{1/2}} [(\tau_1 + \tau_2 + \ldots \tau_n)^{1/2} - R(\tau_2 + \ldots \tau_n)^{1/2} + \ldots R(\tau_n)^{1/2}] \quad (5)$$

These equations can be rearranged into a more convenient form using the following:

$$\frac{nF(D_O\pi)^{1/2}}{2i_{Red}} C^\circ_O = \tau_1^{1/2} \quad (6)$$

$$\tau_n = a_n\tau_1 \quad (7)$$

where a_n is the nth transition time, τ_n, relative to τ_1, (for example, for the well known case of the first reversal, $a_n = 1/3$). Equations 3 and 5 become

$n = 3, 5, 7 \ldots$

$$1 = (a_1 + a_2 + \ldots a_n)^{1/2} - R(a_2 + \ldots a_n)^{1/2} + \ldots R(a_n)^{1/2} \quad (8)$$

$n = 2, 4, 6 \ldots$

$$\frac{D_R^{1/2}C^\circ_R}{D_O^{1/2}C^\circ_O} = (a_1 + a_2 + \ldots a_n)^{1/2} - R(a_2 + \ldots a_n)^{1/2} + \ldots R(a_n)^{1/2} \quad (9)$$

Where $a_1 = 1$, and values for a_2, $a_3 \ldots a_n$ can be obtained by solving (8) and (9). Since these equations can only be solved by an iterative method for n greater than 2, a program for generating Equations 8 and 9, and solving them for successive values of a_n, on a digital computer was prepared (Appendix II). Some computed values of a_n, assuming $D_R = D_O$, for different R's and C°_R/C°_O ratios are listed in Table I.

Figure 3. Cyclic chronopotentiograms of reduction of silver(I) and cadmium(II)

Upper curve. Solution contained 1.71mM cadmium(II) and 0.1M KCl. Current density was 0.370 ma. per sq. cm. at mercury pool electrode.

Lower curve. Solution contained 9.8mM silver(I) and 0.2M KNO₃. Current density was 0.865 ma. per sq. cm. at platinum disk electrode.
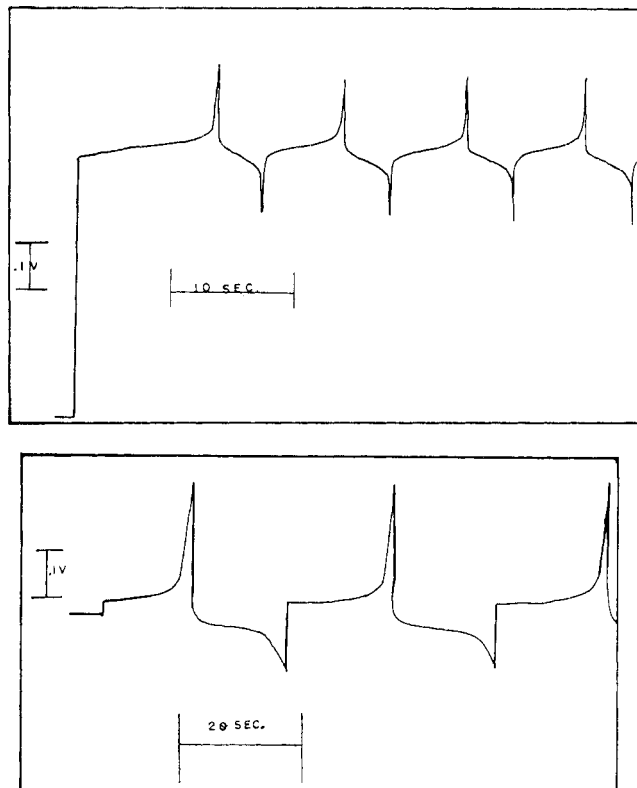
When the reduced species is insoluble and plates onto the electrode, the even-number a_n's (oxidations) are calculated by the equation:

$$n = 2, 4, 6 \ldots$$

$$a_n = \frac{i_{Red}}{i_{Ox}} a_{n-1} \qquad (10)$$

while the odd-numbered a_n's are still calculated by (8). Some computed values for a_n's under these conditions are also listed in Table I.

To give a physical picture of the concentration gradients during CC, consider the case where $C^0{}_R = 0$, and $i_{Ox} = i_{Red}$. During the first reduction C_O ($x = 0$) decreases to zero at τ_1. On reversal, R produced during the first transition diffuses back to the electrode, and when C_R at the electrode surface is zero, $\tau_2 = \tau_1/3$ (or $a_2 = {}^1/_3$). At this point C_O ($x = 0$) is essentially equal to the bulk concentration of the oxidized species, $C^0{}_O$. However, as we move away from the electrode surface, we find that the concentration profile for the oxidized species shows a dip before again assuming its bulk value. Therefore, the transition time for the next reduction, τ_3, is smaller than that initially. For additional scans, the odd scans continuously decrease and the even scans increase.

For the case of an insoluble product the analysis is slightly different. The transition time for the second scan is exactly the same as the first, because the reduced product has not diffused away from the electrode surface. Since during this second scan, oxidized species diffused toward the electrode from the bulk of the solution, the amount of oxidized material in the vicinity of the electrode at the second transition time is larger than that initially present, and hence τ_3 will be larger than τ_1. For additional scans, the transition times continually increase, with every even transition time equal to the preceding odd one.

RESULTS AND DISCUSSION

The theoretical results were experimentally verified by performing CC on three systems. The reduction of cadmium(II) in 0.1M potassium chloride at a mercury electrode, forming cadmium amalgam, and the reduction of iron(III) in 0.2M potassium oxalate at a mercury electrode illustrate processes

in which the products of the electrode reaction are soluble either in the solution or the electrode. The reduction of silver(I) in 0.2M potassium nitrate at a platinum electrode is a process in which the electrode reaction product plates on the electrode. Typical cyclic chronopotentiograms, employing automatic current reversal, are shown in Figure 3. Some typical values for a_n, for the different systems, as well as the theoretical points, are shown in Figure 4. The agreement between experiment and

theory was quite good in all cases. Deviation from theory at higher n-values is probably due to convection, since transition times were usually between 10 and 20 seconds' duration (2). Note that even in the experiments with the shielded platinum electrode of the proper orientation for a single scan (diffusion upward) the concentration of silver ion in the vicinity of the electrode becomes higher than in the bulk of the solution during the second scan, causing density gradients and convec-

Table I. Relative Transition Times for Cyclic Chronopotentiometry under Various Conditions

	Both O and R Soluble			R Insoluble
	$i_{Red} = i_{Ox}$ $C^0{}_R = 0$	$i_{Red} = 2.414 i_{Ox}$ $C^0{}_R = 0$	$i_{Red} = i_{Ox}$ $C^0{}_R = C^0{}_O$	$i_{Red} = i_{Ox}$
n	a_n	a_n	a_n	a_n
1	1.000	1.000	1.000	1.000
2	0.333	1.000	1.778	1.000
3	0.588	0.729	1.713	1.174
4	0.355	1.124	1.740	1.174
5	0.546	0.698	1.724	1.263
6	0.366	1.184	1.735	1.263
7	0.525	0.684	1.727	1.319
8	0.373	1.222	1.733	1.319
9	0.513	0.675	1.728	1.359
10	0.378	1.249	1.732	1.359
11	0.504	0.670	1.728	1.390
12	0.382	1.269	1.732	1.390
13	0.498	0.665	1.729	1.414
14	0.385	1.285	1.732	1.414
15	0.493	0.662	1.729	1.434
16	0.388	1.298	1.731	1.434
17	0.489	0.659	1.729	1.450
18	0.390	1.309	1.731	1.450
19	0.486	0.657	1.730	1.464
20	0.392	1.318	1.731	1.464

tion. The experimental arrangement is currently being modified to allow CC with much shorter transition times to be carried out.

CC for a single system allows transition time data at a given current density to be collected rather rapidly, without repeatedly waiting for the solution to come to rest after each trial and subsequent stirring, subject to limitations due to convection. On the other hand, hopes that later transitions will give correct values even if initial ones are perturbed, for example by accidental stirring, are unfounded. If the first reversal was high, all subsequent scans were high, and vice-versa.

The preceding treatment assumed that the system was chemically (but not necessarily electrochemically) reversible. Information concerning the electrochemical reversibility of the electrode reaction can be gained by the usual comparisons of potentials on the various scans. Subsequent communications will deal with kinetic and catalytic effects and multicomponent systems.

APPENDIX I

Proof of the Murray-Reilley "response function additivity" principle.

Current Response Functions. Using Fick's equation for linear diffusion, and the usual initial boundary conditions for C_o, the following equation can be derived (7)

$$C_O(0, t) = C^{\circ}_o -$$
$$[nF(\pi D_O)^{1/2}]^{-1} \int_O^t i_f(\Theta)(t - \Theta)^{-1/2}d\Theta$$

$$(1a)$$

where $i_f(t)$ is an arbitrary current function, and Θ is a dummy variable of the integration. A general current program, in which the current undergoes step functional changes at time t_1, t_2, etc., is

$$i_f(t) = i_0(t) +$$
$$S_{t_1}(t)i_1(t) +$$
$$S_{t_2}(t)i_2(t) + \ldots \quad (2a)$$

where $S_K(t)$ is the step function, equal to zero when t is between 0 and K, and equal to one when t is larger than K. Therefore

$$C_O(0, t) =$$
$$C^{\circ}_o - [nF(\pi D_O)^{1/2}]^{-1}\Bigg[\int_O^t i_0(\Theta)$$
$$(t - \Theta)^{-1/2}d\Theta +$$
$$\int_O^t S_{t_1}(\Theta)i_1(\Theta)(t - \Theta)^{-1/2}d\Theta +$$
$$\int_O^t S_{t_2}(\Theta)i_2(\Theta)(t - \Theta)^{-1/2}d\Theta + \ldots\Bigg] \quad (3a)$$
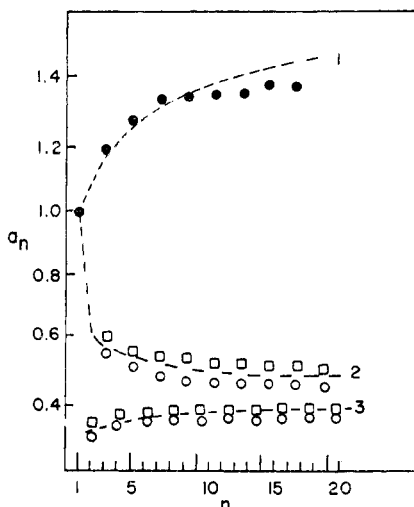

Figure 4. Theoretical and experimental relative transition times for cyclic chronopotentiometry

– – – – theoretical values
1   reductions, insoluble product
2   reductions, soluble product
3   oxidations, soluble product
●   silver(I)—silver metal system
○   cadmium(II)—cadmium amalgam system
□   iron(III)—iron(II) system

Since (3)

$$\int_O^t S_K(\Theta)F(t - \Theta)d\Theta = 0$$

when $0 < t < K$

$$= \int_K^t F(t - \Theta)d\Theta = \int_O^{t-K} F(\lambda)d\lambda$$

when $t > K$ (4a)

(letting $\lambda = t - \Theta$) (3a) becomes

$$C_O(0, t) = C^{\circ}_o -$$
$$[nF(\pi D_O)^{1/2}]^{-1}\Bigg[\int_O^t i_0(t - \lambda)\lambda^{-1/2}d\lambda +$$
$$\int_O^{t-t_1} i_1(t - \lambda)\lambda^{-1/2} d\lambda +$$
$$\int_O^{t-t_2} i_2(t - \lambda)\lambda^{-1/2}d\lambda + \ldots\Bigg] \quad (5a)$$

This can be rewritten as

$$nFD_O^{1/2}[C^{\circ}_o - C_O(0, t)] =$$
$$Z_0(0, t) + Z_1(0, t - t_1) +$$
$$Z_2(0, t - t_2) + \ldots \quad (6a)$$

Where

$$Z_p(0, t - t_p) =$$
$$\pi^{-1/2} \int_O^{t-t_p} i_p(t - \lambda)\lambda^{-1/2}d\lambda \quad (7a)$$

[Reference (5), Equation 31] and are the Murray-Reilley current impulse response functions for linear diffusion.

Note that for constant currents,

$$i_p(t - \lambda) = \beta_p \quad (8a)$$

$$Z_p(0, t - t_p) =$$
$$\beta_p\pi^{-1/2} \int_O^{t-t_p} \lambda^{-1/2}d\lambda =$$
$$2\beta_p\pi^{-1/2}(t - t_p)^{1/2} \quad (9a)$$

which yields Equation 38 in (5).

Surface Concentration Response Functions. For a multicomponent system, the total current can be represented by a sum of the instantaneous currents due to each species,

$$i_f(t) = [b_1(t) + b_2(t) + \ldots] i_f(t) \quad (10a)$$

where $b_1(t)$ is the fraction of the total current at time t causing electrolysis of species 1, etc. Then from (1a), for species m

$$C_m(0, t) = C^{\circ}_m -$$
$$[n_mF(\pi D_m)^{1/2}]^{-1} \int_O^t b_m(\Theta)i_f(\Theta)$$
$$(t - \Theta)^{-1/2}d\Theta \quad (11a)$$

or summing over j species

$$\sum_{m=1}^j n_mFD_m^{1/2}[C^{\circ}_m - C_m(0, t)] =$$
$$\pi^{-1/2} \int_O^t \sum_{m=1}^j b_m(\Theta)i_f(\Theta) (t - \Theta)^{-1/2}d\Theta$$

$$(12a)$$

or, using (10a),

$$\sum_{m=1}^j n_mFD_m^{1/2}[C^{\circ}_m - C_m(0, t)] =$$
$$\pi^{-1/2} \int_O^t i_f(\Theta) (t - \Theta)^{-1/2}d\Theta \quad (13a)$$

Combination of this equation with the results for the current response function above, leads to Equation 1. Equation 1 was essentially proved by Testa and Reinmuth (8), using different notation, for constant currents. The proof given here demonstrates that the equation also holds for step-functional changes with varying (programmed) currents as well.

APPENDIX II

Computer Program for Generating and Solving Equation for CC of Single Component System. The writing and solving of Equations 8 and 9 is quite difficult, since the nth equation contains n terms, and cannot be solved explicitly for a_n. The following Fortran 60 program is designed to generate the equations and solve for the various a_n's. The following data are read in: K the total number of reversals desired, NOSIG, the number of significant figures desired in a_n, $(i_{Red} + i_{Ox})/i_{Red}(RR)$, and C°_o/C°_R (FRACT). and a_n $[T(n)]$ — values are calculated and printed, for n's of 1 to K.

```
C  1 CYCLIC CHRONO, DIFFU-
        SION CONTROL, PLANE
        ELECTRODE, READ IN K
        NOSIG RR FRACT, TWO
        SOLUBLE SPECIES
        READ 900,K,NOSIG, RR,
        FRACT
        DIMENSION X(100),T(100),
        R(100)
C       GENERATION OF EQUA-
        TIONS
        DO 200 N = 1,K
        T(N) = 0.0
        M = 1
        LA = 0
   10   DO 80 I = 1,N
        SUM = 0.0
        DO 60 J = I,N
   60   SUM = SUM + T(J)
        X(I) = SQRTF(SUM)
   80   CONTINUE
        Y = X (1) - 1.0
        IF (1 - N) 81,96,300
   81   SIGN = 1.0
        DO 95 L = 2,N
        SIGN = -SIGN
   95   Y = Y + SIGN * RR * X(L) -
        SIGN - SIGN * FRACT
```

```
C  2 SOLVE GENERATED EQUA-
        TION BEGIN AT 96 READ
        IN NOSIG FOR ACCURACY
   96   IF(M-1)300,100,102
  100   Z = Y
        M = M + 1
  102   IF (Z) 98,200,99
   98   IF (Y) 71,200,73
   99   IF (Y) 73, 200, 71
   71   T(N) = T(N) + 10.0 **(-LA)
        GO TO 10
   73   T(N) = T(N) - 10.0 **(-LA)
        LA = LA + 1
  199   IF (NOSIG - LA) 300,200, 71
  200   CONTINUE
C  3 EQUATION SOLVED PRINT
        ANSWER
        DO 201 J = 1,K,2
  201   R(J) = T(J)/T(J + 1)
        PRINT 903, RR, FRACT
        PRINT 901
        PRINT 902, [N,T(N),R(N),
        N = 1,K]
  500   CONTINUE
  900   FORMAT (2I10, 2F10.5)
  901   FORMAT [4(3X, 1HN, 6X,
        4H TAU, 5X, 5HRATIO)//]
  902   FORMAT [4(1X, 1I3, 2F10.6)/]
```

```
  903   FORMAT (5HRR =, F10.5,
        8HFRACT =, F10.5)
        GO TO 920
  300   PRINT 905
  905   FORMAT (2X,5HERROR)
  920   STOP
        END
        END
```

LITERATURE CITED

(1) Alden, J. R., Chambers, J. Q., Adams, R. N., *J. Electroanal. Chem.* **5**, 152 (1963).
(2) Bard, A. J., ANAL. CHEM. **33**, 11 (1961).
(3) Churchill, R. V., "Operational Mathematics," p. 39, McGraw-Hill, New York, 1958.
(4) Galus, Z., Lee, H. Y., Adams, R. N., *J. Electroanal. Chem.* **5**, 17 (1963).
(5) Murray, R. W., Reilley, C. N., *Ibid.*, **3**, 182 (1962).
(6) Piette, L. H., Ludwig, P., Adams, R. N., ANAL. CHEM. **34**, 916 (1962).
(7) Reinmuth, W. H., *Ibid.*, **34**, 1446 (1962).
(8) Testa, A. C., Reinmuth, W. H., *Ibid.*, **33**, 1324 (1961).

High Speed Controlled Potential Coulometry

ALLEN J. BARD

Department of Chemistry, The University of Texas, Austin, Texas

▶ An electrolysis cell for rapid controlled potential coulometric determinations, employing a large electrode area-to-solution volume ratio and using ultrasonic and nitrogen stirring, was designed. This cell allowed determinations to be performed with total electrolysis times of less than 100 seconds. The apparatus was tested by determining silver (I) and iodide by electrodeposition of silver and silver iodide, respectively. From 2.5 to 25 μmoles of each was determined with an average error of 2 to 0.2%. The application of this cell to the study of mechanisms of electrode reactions was also considered.

CONTROLLED potential coulometry has been useful both as an analytical technique and for the investigation of mechanisms of electrode reactions. The time required to perform a controlled potential determination is usually between 20 minutes and 2 hours, depending upon the experimental apparatus employed. Although controlled potential coulometric analysis has the advantage of being an absolute method—i.e., allowing the direct determination of the quantity of a substance without reference to calibration curves, etc.—the long electrolysis times usually required sometimes discourage potential users of this technique. The aim of this study was to consider the factors governing the speed of an electrolysis, and to design a cell capable of performing a controlled potential coulometric analysis in a short time.

For a single electrode reaction carried out at potentials at which the rate of the reaction is limited by the rate of mass transfer of the electroactive species to the electrode, the current decays according to the equation (7)

$$i_t = i_0 e^{-pt} \qquad (1)$$

where i_t is the current at time t, i_0 is the initial current, and p is a function of the electrode dimensions, solution volume, cell geometry, and rate of mass transfer. For a simple Nernst diffusion layer model of convection, p is given by the expression

$$p = DA/\delta V \qquad (2)$$

where D is the diffusion coefficient of the electroactive species, A is the electrode area, V is the total solution volume, and δ is the thickness of the diffusion layer. The actual dependence of p upon these variables is very complex, and depends upon such experimental conditions as electrode shape, cell geometry, and turbulence of flow. It is probably better to write simply

$$p = f(A, 1/V, m) \qquad (3)$$

where m is a mass transfer constant. There is frequently no direct proportionality between p and A; the dimensions of the electrode, rather than the area, are more important (3). Completion of electrolysis is generally taken at the time when the current has decayed to 0.1% of its initial value, that is

$$t = 6.9/p \qquad (4)$$

To decrease the electrolysis time, p must be made as large as possible. In this study an electrolysis cell was designed with a large electrode area-to-solution volume ratio, which employed ultrasonic and nitrogen stirring. With this cell an "effective p" of about 0.1 second^{-1} was obtained, so that electrolysis times were only slightly longer than one minute.

EXPERIMENTAL

Apparatus. With a suitable potentiostat and coulometer, the design of the electrolysis cell usually governs the electrolysis time. After experi-