Cyclic Chronopotentiometry

Multicomponent Systems and Stepwise Reactions

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▶ Cyclic chronopotentiometry is applied to mathematically equivalent cases—multicomponent systems and stepwise reactions in a single component system. The equations for the successive transition times have been derived and solved. The reduction of a mixture of lead and cadmium ions and the stepwise reduction of copper ion at a mercury pool electrode confirmed the theoretical calculations. The theoretical results were used to calculate the half-wave potential on each scan of a single component system and the reduction of lead ion was used to confirm these results.

CONSTANT CURRENT chronopotentiometry was first applied to a multicomponent system and a stepwise reaction by Berzins and Delahay (1, 3). The following cases were treated with linear diffusion conditions being assumed.

Multicomponent system

$$A + n_1e \rightleftharpoons B \qquad (1)$$

$$C + n_2e \rightleftharpoons D \qquad (2)$$

Stepwise reaction

$$A + n_1e \rightleftharpoons B \qquad (3)$$

$$B + n_2e \rightleftharpoons C \qquad (4)$$
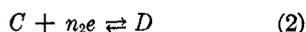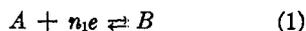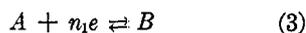
These authors derived the flux after the transition time of the first component, τ, and used this to calculate the flux and subsequent transition time of the second species. The derivation was extended by Kambara and Tachi (7) to an arbitrary number of reducible species.

Similar results have been derived for cylindrical electrodes (11) and for current varying with the square root of time (6). Murray and Reilley (9) have shown how these results, and many more, can be derived from the surface concentration response function additivity principle. A proof of the response function additivity principle has been presented (4).

The application of step functional changes in current to multicomponent systems has been treated by Testa and Reinmuth (13) and experimentally

verified by them. Palke, Russel, and Anson (10) have derived the equation for the first transition time, after reversal of current, in a two-component system. Their results were confirmed with several systems. Murray and Reilley (9) have shown how these results can also be derived through the use of their current response function additivity principle.

Cyclic chronopotentiometry (CC), a special case of programmed current chronopotentiometry where the constant current is reversed at each transition time, has been applied to single-component systems with both diffusion control (4) and with subsequent chemical reactions (5). The method was shown to be experimentally convenient and to give more information than methods involving only a single transition time measurement or one reversal of current.

In this paper, the method is applied to multicomponent systems and stepwise reactions. Theoretical equations for cyclic chronopotentiometry were derived using the response function additivity principle and were solved for the actual transition times with a computer. The theoretical results were confirmed experimentally. In addition, the suggestion (10) that for a single component system the half-wave potential after each reversal can be calculated from the transition times for a multicomponent system has been verified.

EXPERIMENTAL

The instrumentation for CC has been described (4, 5). The transition times were taken from the recorded potential-time curves. The odd-number transition times were taken at the point where the curve became linear, and the even numbered ones, from the point of reversal. The potential axis of the recorder was expanded to about 0.4 volt for accurate half-wave potential measurements.

The solutions were made up approximately from aliquots of previously standardized stock solutions and were at room temperature (25° ± 1° C.). Prepurified nitrogen was used to deaerate solutions for at least 15 minutes.

THEORETICAL

Multicomponent Systems. Theoretical equations for cyclic chronopotentiometry on a multicomponent system are conveniently derived using the Murray-Reilley (9) response functions. This is mathematically expressed as

$$\sum_m n_m F D_m^{1/2}[C_m{}^\circ - C_m(0, t)] = \sum_p Z_p(0, t - t_p) \qquad (5)$$

where $C_m{}^\circ$ is the initial concentration of the mth species, $C_m(0, t)$ is its concentration at the electrode surface at time t, $Z_p(0, t - t_p)$ is the current impulse function, and the other symbols have their usual meaning. This expression is derived from the fact that the sum of the instantaneous currents caused by each species is equal to the applied current function. Using the zero shift theorem of the Laplace transformation (2), it can be shown that (4)

$$Z_p(0, t - t_p) = \pi^{-1/2} \int_0^{t - t_p} i_p(t - \lambda)\lambda^{-1/2}d\lambda \quad (6)$$

When a constant current, $i_p = \beta$, is applied, the integral in Equation 6 takes the form

$$Z_p(0, t - t_p) = 2\beta\pi^{-1/2}(t - t_p)^{1/2} \quad (7)$$

Consider the reduction of a two-component system corresponding to Equations 1 and 2 in a solution containing A and C, at concentrations of $C_A{}^\circ$ and $C_C{}^\circ$ respectively, with no B and D present, where A and C are reduced at sufficiently different potentials to yield a potential-time curve exhibiting two distinct steps. At the first transition time, τ_1, $C_A(0, \tau_1) = 0$. Thus, Equation 5 becomes

$$K_A C_A{}^\circ = \tau_1^{1/2} \qquad (8)$$

where

$$K_m = \frac{n_m F D_m^{1/2}\pi^{1/2}}{2i_{red}} \qquad (9)$$

The symbols have their usual meaning; i is the current density.

At the second transition time, τ_2,

$C_C(0, \tau_2) = 0$. Thus, Equation 5 now becomes

$$K_C C_C{}^\circ + K_A C_A{}^\circ = (\tau_1 + \tau_2)^{1/2} \quad (10)$$

At the third transition time, τ_3, the first reversal

$$C_A(0, \tau_3) = 0,\ C_D{}^\circ = 0,$$
$$\text{and } C_D(0, \tau_3) = 0.$$

Thus Equation 5 becomes

$$K_A C_A{}^\circ = (\tau_1 + \tau_2 + \tau_3)^{1/2} - R\,\tau_3{}^{1/2} \quad (11)$$

where R equals the change in current, $(i_{red} + i_{ox})/i_{red}$. When the reversal current is equal and opposite to the

Table I. Relative Transition Times for Cyclic Chronopotentiometry of Two-Component System or Two-Step Reaction of Single Component

(All species soluble and reduced forms initially absent)

	a_n			
	$i_{red} = i_{ox}$ $K_A C_A{}^\circ = K_C C_C{}^\circ$ or $n_1 = n_2$	$i_{red} = i_{ox}$ $K_A C_A{}^\circ = 2 K_C C_C{}^\circ$ or $n_1 = 2 n_2$	$i_{red} = i_{ox}$ $K_C C_C{}^\circ = 2 K_A C_A{}^\circ$ or $n_2 = 2 n_1$	$i_{red} = 2 i_{ox}$ $K_A C_A{}^\circ = K_C C_C{}^\circ$ or $n_1 = n_2$
n				
1	1.000	1.000	1.000	1.000
2	3.000	1.250	8.000	3.000
3	0.286	0.068	1.204	0.577
4	1.047	0.682	1.796	2.623
5	0.375	0.440	0.322	0.561
6	1.977	0.882	4.970	2.246
7	0.297	0.070	1.260	0.611
8	1.123	0.728	1.933	2.941
9	0.361	0.417	0.315	0.545
10	1.822	0.811	4.597	2.126
11	0.301	0.071	1.288	0.625
12	1.162	0.752	2.004	3.100
13	0.355	0.407	0.312	0.538
14	1.747	0.776	4.418	2.070
15	0.304	0.071	1.305	0.634
16	1.187	0.768	2.051	3.201
17	0.351	0.400	0.310	0.534
18	1.701	0.754	4.308	2.035
19	0.306	0.071	1.317	0.639
20	1.206	0.779	2.085	3.273

Table II. Time for Potential of Single Component System to Equal Polarographic Half-Wave Potential

(Time is expressed as a ratio of τ_n)

	$(t_n/\tau_n)_{E=E_{1/2}}$			
n	$i_{red} = i_{on}$	$i_{red} = 2 i_{ox}$	$i_{red} = 4 i_{ox}$	$i_{red} = 1.333\ i_{ox}$
1	0.250	0.250	0.250	0.250
2	0.215	0.180	0.136	0.202
3	0.159	0.200	0.225	0.178
4	0.209	0.172	0.126	0.195
5	0.165	0.204	0.228	0.183
	0.206	0.168	0.121	0.192
	0.169	0.206	0.229	0.186
	0.204	0.165	0.118	0.189
	0.171	0.208	0.230	0.188
10	0.203	0.163	0.116	0.188

forward current, R equals 2. At the fourth transition time, $C_B{}^\circ = 0$, $C_B(0, \tau_4) = 0$, $C_D{}^\circ = 0$, and $C_D(0, \tau_4) = 0$; thus Equation 5 becomes

$$0 = (\tau_1 + \tau_2 + \tau_3 + \tau_4)^{1/2} - R(\tau_3 + \tau_4)^{1/2} \quad (12)$$

This process is continued in a similar manner for the subsequent transition times. The general equations are:

$n = 1, 5, 9 \ldots$

$$K_A C_A{}^\circ = (\tau_1 + \tau_2 + \ldots \tau_n)^{1/2} - R(\tau_3 + \ldots \tau_n)^{1/2} + \ldots + R\tau_n{}^{1/2} \quad (13)$$

$n = 2, 6, 10 \ldots$

$$K_A C_A{}^\circ + K_C C_C{}^\circ = (\tau_1 + \tau_2 + \ldots \tau_n)^{1/2} - R(\tau_3 + \ldots \tau_n)^{1/2} + \ldots + R(\tau_{n-1} + \tau_n)^{1/2} \quad (14)$$

$n = 3, 7, 11 \ldots$

$$K_A C_A{}^\circ = (\tau_1 + \tau_2 + \ldots \tau_n)^{1/2} - R(\tau_3 + \ldots \tau_n)^{1/2} + \ldots - R\tau_n{}^{1/2} \quad (15)$$

$n = 4, 8, 12 \ldots$

$$0 = (\tau_1 + \tau_2 + \ldots \tau_n)^{1/2} - R(\tau_3 + \ldots \tau_n)^{1/2} + \ldots - R(\tau_{n-1} + \tau_n)^{1/2} \quad (16)$$

As Testa and Reinmuth (13) pointed out, the third transition time is unusual; species A is reduced during an oxidation scan and the third transition time is abnormally low.

These equations can be shown to be independent of the first transition time by making the substitution $a_n = \tau_n/\tau_1$, as was done in a previous communication (4). For example, the general transition time equations now become $n = 1, 3, 5 \ldots$

$$1 = (a_1 + a_2 + \ldots a_n)^{1/2} - R(a_3 + \ldots a_n)^{1/2} + \ldots R(a_n)^{1/2} \quad (17)$$

$n = 2, 6, 10 \ldots$

$1 + K_C C_C{}^\circ / K_A C_A{}^\circ$

$n = 4, 8, 12 \ldots$

0

$$\left. \vphantom{\begin{array}{c}1\\1\\0\end{array}} \right\} =$$

$$(a_1 + a_2 + \ldots a_n)^{1/2} - R(a_3 + \ldots a_n)^{1/2} + \ldots R(a_{n-1} + a_n)^{1/2} \quad (18)$$

The Fortran computer program used in the numerical solution of these equations is listed in Appendix I. Table I gives the values calculated for various values of $K_C C_C{}^\circ / K_A C_A{}^\circ$ and R. The overall reduction and oxidation scans reduce to the diffusion controlled relative transition times for one species (4). Thus $(a_3 + a_4)/(a_1 + a_2) = 1/3$. This program is not useful for treating a single component system by setting $K_C C_C{}^\circ / K_A C_A{}^\circ$ equal to zero. Because of the finite number of significant figures

calculated, a small negative transition time may be obtained under these conditions which cannot be handled by the program.

Stepwise Reactions. The theoretical treatment of a stepwise reaction is essentially identical to that of the multicomponent system (10). A proof of this statement is shown in Appendix II. In Equation 18, the general equation for the relative transition times, $K_C C_C{}^\circ / K_A C_A{}^\circ$ is replaced by n_2/n_1. The same computer program can then be used to calculate the transition times for a stepwise reaction of a single species (Table I).

Half-Wave Potentials. It has also been stated (10) that the polarographic half-wave potentials of a single component cyclic chronopotentiogram— that is, the potential when $D^{1/2}{}_{ox} C_{ox}(0, t) = D^{1/2}{}_{red} C_{red}(0, t)$—can be calculated from the transition times of a two-step reaction when $n_2 = n_1$. The half-wave potential of any scan occurs at the relative time calculated from the relation $n = 1, 2, 3 \ldots$

$$(t_n/\tau_n)_{E=E_{1/2}} = a_{2n-1}/(a_{2n-1} + a_{2n}) \quad (19)$$

where the a's are calculated from the stepwise reaction case where $n_1 = n_2$. A proof of Equation 19 is shown in Appendix III. Table II gives the values of $(t_n/\tau_n)_{E=E_{1/2}}$ for equal forward and reverse currents and other cases. For the first reversal, the results agree with the values calculated from the exact equation derived by Macero and Anderson (8).

RESULTS AND DISCUSSION

The theoretical results for the multi-component system were confirmed for the reduction of a mixture of lead(II) and cadmium(II) ions at a mercury electrode; the products, metallic cadmium and lead, are soluble in the mercury. A typical cyclic chronopotentiogram is shown in Figure 1. The experimental results are tabulated in Table III and compared with the theoretical calculations. The overall transition time ratios followed the simple diffusion case previously discussed (4). The observed first and second transition times were used to calculate $K_C C_C{}^\circ / K_A C_A{}^\circ$ (FRACT) using the relationship

$$K_C C_C{}^\circ / K_A C_A{}^\circ = (1 + a_2)^{1/2} - 1 \quad (20)$$

This value was then used to calculate the theoretical transition times ratios for comparison with the experimental results. Deviations from the theoretical results became noticeable after sixty seconds, probably because of convection.

In one series of experiments involving lead and cadmium in a chloride medium,

the solubility product of lead chloride was inadvertently exceeded. Although the first four transitions were apparently normal, the fifth and subsequent reversals deviated from the theoretical calculations. This ability to notice deviations points to one advantage of cyclic chronopotentiometry; errors and effects that might remain unsuspected when chronopotentiometric techniques involving only a single reversal are applied become apparent in CC.

The theoretical results for the stepwise reaction system were confirmed experimentally for the reduction of copper(II) ion in an ammoniacal medium on a mercury pool electrode. In this medium, copper(II) is reduced in two steps, first to copper(I) and then to the metal. Both copper(I) and copper(II) ions are soluble in the solution and copper metal is soluble in
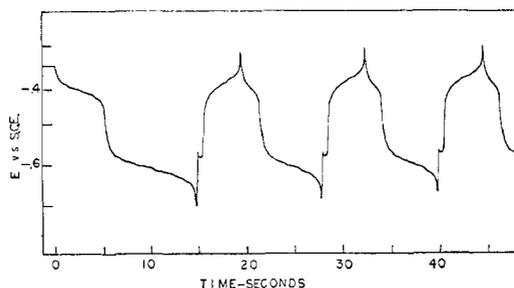
Figure 1. Cyclic chronopotentiogram for the reduction of a lead(II) and cadmium(II) mixture. Conditions are the same as in Table III

the mercury. The experimental results and comparison with the calculations for n_1 equal to n_2 (FRACT = 1) are shown in Table IV.

A cyclic chronopotentiogram for the reduction of lead(II) ion in 0.05M nitric acid was used to measure half-wave potentials to confirm the results in Table II. Three forward scans on a mercury pool electrode at a current

Program in Fortran 60

```
C   1   CYCLIC CHRONO, MULTIPLE COMPONENT SYSTEM, PLANE ELECTRODE,
C       DIFFUSION CONTROL, TWO SOLUBLE SPECIES, NO REDUCED FORM
        DIMENSION X(100), T(100), R(100)
        READ 900, K, NOSIG, RR, FRACT
C       GENERATION OF EQUATIONS
        DO 200 N = 1, K
        T(N) = 0.0
        M = 1
        LA = 0
    10  DO 80 I = 1, N, 2
        SUM = 0.0
        DO 60 J = I, N
    60  SUM = SUM + T(J)
        X(I) = SQRTF(SUM)
    80  CONTINUE
        Y = X(I) — 1.0
        IF (2 — N) 81, 33, 96
    81  SIGN = 1.0
        DO 95 L = 3, N, 2
        SIGN = —SIGN
    95  Y = Y + SIGN * RR * X(L)
        IF (XMODF(N, 2)) 300, 31, 96
    31  IF (XMODF(N, 4)) 300, 32, 33
    32  Y = Y + 1.0
        GO TO 96
    33  Y = Y — FRACT
C   2   SOLVE GENERATED EQUATION 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 ((T(N)/10.0**(—LA)) — 10.0 **(NOSIG)) 71, 200, 200
   200  CONTINUE
C   3   EQUATION SOLVED PRINT ANSWER
        DO 201 J = 1, K, 2
   201  R(J) = T(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
```

Table III. Relative Transition Times for Cyclic Chronopotentiometry of Two-Component System: Lead(II) and Cadmium(II)

(Solution contained 5mM lead(II), 3.4 mM cadmium(II), 0.1M HClO$_4$, and 0.05M HNO$_3$. Current density was 1.00 ma. per square cm. at a mercury pool electrode. τ_1 was 5.2 seconds)

	a_n (individual)		a_n (overall)	
n	Exp.	Theor.	Exp.	Theor.
1	1.00	(1.00)	1.00	1.00
2	1.66	(1.66)		
3	0.11	0.11	0.34	0.33
4	0.77	0.78		
5	0.40	0.42	0.57	0.59
6	1.12	1.15		
7	0.13	0.11	0.35	0.36
8	0.79	0.83		
9	0.38	0.40	0.54	0.55
10	1.04	1.05		
11	0.13	0.11	0.36	0.37
12	0.82	0.86		
13	0.37	0.39	0.53	0.53
14	1.03	1.01		
15	0.12	0.11	0.36	0.37
16	0.84	0.88		
17	0.38	0.38	0.53	0.51
18	1.04	0.98		
19	0.11	0.12	0.38	0.38
20	0.89	0.89		

Table IV. Relative Transition Times for Cyclic Chronopotentiometry of Copper(II) Undergoing Stepwise Reaction

(Solution contained 5 mM copper(II) chloride, 0.1M NH$_4$Cl, and 0.1M NH$_3$. Current density was 0.68 ma. per square cm. at a mercury pool electrode. τ_1 was 5.7 seconds)

	a_n (individual)		a_n (overall)	
n	Exp.	Theor.	Exp.	Theor.
1	1.00	(1.00)	1.00	1.00
2	3.01	3.00		
3	0.27	0.29	0.34	0.33
4	1.08	1.05		
5	0.37	0.38	0.58	0.59
6	1.97	1.98		
7	0.30	0.30	0.36	0.36
8	1.16	1.12		
9	0.36	0.36	0.55	0.55
10	1.85	1.82		
11	0.28	0.30	0.37	0.37
12	1.20	1.16		
13	0.36	0.36	0.53	0.53
14	1.78	1.75		
15	0.28	0.30	0.38	0.37
16	1.24	1.19		
17	0.36	0.35	0.53	0.51
18	1.79	1.70		
19	0.29	0.31	0.38	0.38
20	1.25	1.21		

density of 0.7 ma. per square cm. gave a half-wave potential of -0.402 volt ± 1 mv., and three reverse scans gave a potential of -0.397 volt ± 1 mv., vs. S.C.E. indicating the correctness of the theoretical calculations. The small disparity between the potentials found on forward and reverse scans can be explained by an apparent resistance of about 1 ohm between the reference electrode tip and the working electrode. Alternately, a small amount of irreversibility could explain the difference. For the first scan of a reversible reaction in chronopotentiometry the following equation holds:

$$E_{3/4} - E_{1/4} = 0.048/n \text{ volt} \quad (21)$$

The measured value for lead ion in this medium was 0.026 volt, which is close to the value 0.024 volt calculated by Equation 21.

APPENDIX I

Computer Program for Generating and Solving Equations for CC of a Multicomponent System, Stepwise Reaction of a Single Component, and Time Corresponding to Half-Wave Potential on Each Scan of a Single Component System. This program in Fortran 60 generates and solves the equations for the various relative transition times. 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 $K_C C_C{}^\circ / K_A C_A{}^\circ$ (or n_2/n_1)(FRACT). The output prints the values of $a_n[T(n)]$ and the ratio $(t_n/ \tau_n)_{E=E1/2}[R(n)]$. If the reduced form of substance A (substance B) is present, add a term to statement 32 corresponding to the ratio $D_B{}^{1/2} C_B{}^\circ / D_A{}^{1/2} C_A{}^\circ$.

Also note that in a previous communication (4) FRACT should read $C_O{}^\circ / C_R{}^\circ$, rather than as given there.

APPENDIX II

Proof of Murray-Reilley Surface Concentration Response Function for the Stepwise Reaction of a Single Component. If a substance A reacts according to the following scheme

$$A + n_1 e \rightarrow B \quad (1a)$$

$$A + (n_1 + n_2)e \rightarrow C \quad (2a)$$

$$B + n_2 e \rightarrow C \quad (3a)$$
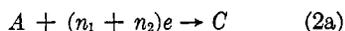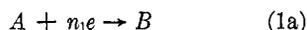
the instantaneous currents caused by reactions 1a to 3a can be defined as $i_1(t)$, $i_2(t)$, and $i_3(t)$, respectively. For example, the special case where the two steps are distinct, $i_1(t) = i_f(t)$ and $i_2(t) = i_3(t) = 0$, for $0 \leq t \leq \tau_1$, where $i_f(t)$ is the total applied programmed current. For $\tau_1 < t \leq \tau_2$, $i_1(t) = 0$ and $i_2(t)$ and $i_3(t)$ are complicated functions of time.

The equations that describe the flux of A and B are

$$D_A(\partial C_A/\partial x)_{x=0} = i_1(t)/n_1 F + i_2(t)/(n_1 + n_2)F \quad (4a)$$

$$D_B(\partial C_B/\partial x)_{x=0} = -i_1(t)/n_1 F + i_3(t)/n_2 F \quad (5a)$$

With the Laplace transformation, the following equations can be derived for the surface concentrations of species A and B:

$$C_A(0, t) = C_A{}^\circ - [n_1 F(D_A \pi)^{1/2}]^{-1} \times \int_0^t i_1(\theta)(t - \theta)^{-1/2} d\theta -$$

$$[(n_1 + n_2)F(D_A \pi)^{1/2}]^{-1} \int_0^t i_2(\theta) \times (t - \theta)^{-1/2} d\theta \quad (6a)$$

$$C_B(0, t) = [n_1 F(D_B \pi)^{1/2}]^{-1} \int_0^t i_1(\theta) \times (t - \theta)^{-1/2} d\theta - [n_2 F(D_B \pi)^{-1/2}]^{-1} \times \int_0^t i_3(\theta)(t - \theta)^{-1/2} d\theta \quad (7a)$$

Multiplying Equation 6a by $(n_1 + n_2) \times FD_A{}^{1/2}$ and Equation 7a by $n_2 FD_B{}^{1/2}$, adding, rearranging, and using the fact that $i_f(t) = i_1(t) + i_2(t) + i_3(t)$ gives

$$(n_1 + n_2)FD_A{}^{1/2}[C_A{}^\circ - C_A(0, t)] - n_2 FD_B{}^{1/2} C_B(0, t) =$$

$$\pi^{-1/2} \int_0^t i_f(\theta)(t - \theta)^{-1/2} d\theta \quad (8a)$$

The results can be expanded to multistep reactions by adding additional terms to the fluxes and surface concentrations of A and B corresponding to the extra steps, and by writing expressions for the flux and surface concentration of any other intermediates. Again, the individual currents must add up to the applied value. The extension to multiple current reversals and other programmed currents is made by using the current response function principle on the right side of Equation 8a, as in Appendix I in (4). A similar proof for constant current chronopotentiometry in a three-step reaction has been given by Testa and Reinmuth (12).

APPENDIX III

Proof of Equivalence between Stepwise Reaction Calculations Where $n_1 = n_2$, and Time Corresponding to Half-Wave Potential of Each Scan in a One-Component System. To show that the half-wave potential on the kth scan of a single component system occurs at the time t_k calculated by the expression $k = 1, 2, \ldots n$,

$$[t_k/\tau_k]_{E=E1/2} = a_{2k-1}/(a_{2k-1} + a_{2k}) \quad (9a)$$

where t_k is measured from the previous transition time, τ_k is the transition time of the kth scan, and the a's are the relative transition times of a stepwise reaction.

In a one-component system, the half-wave potential occurs at the time where

$$D^{1/2}{}_{ox} C_{ox}(0, t) = D^{1/2}{}_{red} C_{red}(0, t) \quad (10a)$$

The response function additivity principle permits writing the following equations for any time, t_n, on the nth scan when $i_{red} = i_{ox}$ and $C_{red}{}^\circ = 0$

$$K_{ox} C_{ox}(0, t) = \tau_1{}^{1/2} - (\tau_1 + \tau_2 + \ldots t_n)^{1/2} + 2(\tau_2 + \ldots t_n)^{1/2} \ldots 2t_n{}^{1/2} \quad (11a)$$

$$K_{red} C_{red}(0, t) = (\tau_1 + \tau_2 + \ldots t_n)^{1/2} - 2(\tau_2 + \ldots t_n)^{1/2} \ldots 2t_n{}^{1/2} \quad (12a)$$

Equating 12a and 11a using 10a, dividing by $\tau_1{}^{1/2}$, and rearranging gives

$$1 = [4(a_1 + a_2 + \ldots A_n)]^{1/2} - 2[4(a_2 + \ldots A_n)]^{1/2} + \ldots 2[4(A_n)]^{1/2} \quad (13a)$$

where a's are the relative transition times and $A_n(t_n/\tau_1)$ is the relative time at which the half-wave potential occurs in the nth transition.

By making the following substitutions into Equation 13a, a result equivalent to the stepwise reaction is obtained:

$$k = 1, 2, \ldots n - 1$$

$$4a_k = a_{2k-1}' + a_{2k}' \quad (14a)$$

and

$$k = n$$

$$4A_k = a_{2k-1}' \quad (15a)$$

yields

$$k = 1, 2, \ldots n$$

$$1 = (a_1' + a_2' + \ldots a_{2n-1}')^{1/2} - 2(a_2' + \ldots a_{2n-1}')^{1/2} + \ldots 2a_{2n-1}'^{1/2} \quad (16a)$$

Equation 16a has the same form as Equation 17 for a stepwise reaction.

The relative transition times for a single component system with no C_R present and $i_{red} = i_{ox}$ has been shown to be [Equations 8 and 9 in (4)]: $n = 1, 2, \ldots$

$$\left. \begin{array}{l} n \text{ odd, } 1 \\ n \text{ even, } 0 \end{array} \right\} = (a_1 + a_2 + \ldots a_n)^{1/2} - 2(a_2 + \ldots a_n)^{1/2} + \ldots 2a_n{}^{1/2} \quad (17a)$$

Multiplying by 2 and substituting in Equation 17a

$$k = 1, 2, \ldots n$$

$$4a_k = a_{2k-1}' + a_{2k}'$$

yields $\quad n = 1, 2, \ldots$

$$\left. \begin{array}{l} n \text{ odd, } 1 \\ n \text{ even, } 0 \end{array} \right\} = (a_1' + a_2' +$$

$$\ldots a_{2n}')^{1/2} - 2(a_2' + \ldots a_{2n}')^{1/2} +$$
$$\ldots 2a_{2n}'^{1/2} \quad (18a)$$

This has the same form as Equation 18 for a stepwise reaction when $n_1 = n_2$. The simultaneous solution of Equations 18a and 16a will give the same results as the stepwise reaction calculations. The substitutions that were used to demonstrate the equivalence between the two sets of equations are 15a and 14a. Dividing Equation 15a by Equation 14a gives the desired relation, 9a.

Thus, the time at which the potential of a single component system equals the polarographic half-wave potential can be calculated from the relative transition times of a stepwise reaction when $n_1 = n_2$.

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Behavior of the Iodide-Iodine Couple at Platinum Electrodes

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▶ Certain electrochemical experiments with the I_2-I^- couple indicate the presence of adsorbed iodine and the absence of adsorbed iodide on platinum electrodes. Radiotracer experiments prove that both iodine and iodide are adsorbed but only the adsorbed iodine is electroactive. None of the previously written mechanisms for the flow of exchange current at platinum electrodes in I_2-I^- solutions is compatible with the results presented.

THE APPARENT ELECTROCHEMICAL reversibility of the iodide-iodine couple at platinum electrodes has prompted a number of studies of the mechanism of the electrode reaction (*13*, *17*, *20*, *31*). In several of the studies (*13*, *17*, *20*), it is asserted that adsorption of iodide or iodine is involved, but there is a divergence of opinion concerning the details of the mechanism (*32*). In a recent study (*26*), the present authors concluded that iodine but not iodide was adsorbed on platinum electrodes because no electroactivity ascribable to adsorbed iodide could be observed. This conclusion was opposed to a number of previous studies (*2–4*, *11*, *14*, *21–3*, *28*) and led the authors to carry out further electrochemical studies and radiotracer experiments with iodine-131 to resolve the contradiction. The radiotracer experiments, which were similar to those described by Kazarinov and

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Balashova (*14*), confirm unequivocally that both iodide and iodine are extensively adsorbed on platinum electrodes. This result, together with the electrochemical experiments reported in our previous study and the present one, force us to conclude that although both iodide and iodine are adsorbed on the electrode only the iodine displays electrochemical activity in the vicinity of the reversible iodide-iodine potential.

EXPERIMENTAL

Radiotracers. Carrier-free iodine-131 was obtained as an aqueous solution of sodium iodide from Tracerlab, Inc. (Richmond, Calif.).

The radiochemical counting techniques followed standard practice. The counting equipment consisted of a well-type thallium-doped sodium iodide crystal, and a single-channel analyzer (R.I.D.L., Melrose Park, Ill.). The 0.33-m.e.v. gamma ray emitted by I^{131} was the radiation that was monitored.

In agreement with Kazarinov and Balashova (*14*) we observed that the adsorption of iodide and iodine was quite irreversible. Very little adsorbed iodide was removed from an electrode by thorough washing with distilled water or sulfuric acid. Accordingly, the amount of iodine (in all oxidation states) adsorbed could be measured simply by counting an electrode that had been exposed to a solution containing I^{131} and then washed free of unadsorbed iodide. It was also possible to follow removal of radioactive iodine from the electrode by counting the electrode or, more sensitively, by counting aliquots of the solution in which desorption was being effected chemically or electrochemically.

Electrochemical. Chronopotentiometric experiments were conventional, although care was taken to avoid shorting the indicator and auxiliary electrodes during switching. When make-before-break mercury-wetted relays are used to switch the constant current from the dummy resistor to the electrochemical cell, the indicator and auxiliary electrodes are shorted together for about 0.5 msecond. Depending on the prior history of the auxiliary electrode, a brief current pulse may flow between the short-circuited electrodes thus destroying the strictly galvanostatic conditions required for chronopotentiometric experiments; various solutions to this problem have been proposed (*1*, *8*). In the present work a switching box utilizing break-before-make relays was employed. Transition times were determined by the method suggested by Voorhies and Furman (*33*). It is likely that the better switching circuitry and the graphical method used to determine the

Table I. Chronopotentiometric Data for Iodine Reduction

0.010F KI, 0.001F I_2, 1F H_2SO_4
0.2 sq. cm. Pt button electrode

Current, μa.	τ (cathodic), seconds	$i\tau^{1/2}$, μa.-second$^{1/2}$
51	7.10	136
75	3.45	139
115	1.58	145
185	0.69	154
285	0.345	168
525	0.116	179
825	0.057	197
1325	0.0285	224
1625	0.0210	236
2925	0.0082	265