known sample on each chromatogram.

Apparently, the paper chromatographic conditions are not adequately controlled, so that an individual calibration curve for each chromatogram is necessary. The variations in calibration curves from one chromatogram to the next are demonstrated in Figure 1. A good linear relation exists for each chromatogram but the slope varies from one chromatogram to the next.

Table IV shows that the standard deviation for the determination of α,α'-diglycerol is ±10%. The accuracy of the method is of the same order of magnitude as the precision, as shown in Table III.

The possibility was considered that relatively large amounts of glycerol significantly alter the areas of α,α'-diglycerol. Accordingly, varying amounts of α,α'-diglycerol were chromatographed in mixture with glycerol. The areas of the α,α'-diglycerol spots were compared with those obtained by chromatographing the α,α'-diglycerol as a pure compound. The results summarized in Table V indicate that glycerol does not affect the areas of the α,α'-diglycerol.

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Model for Current Reversal Chronopotentiometry with Second-Order Kinetic Complications

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▶ **A model has been developed for the analysis of current reversal chronopotentiograms in systems where the electrode process is followed by a homogeneous second-order reaction. The model is analyzed using the IBM 7094 digital computer programmed in Fortran language. Working curves, derived with the aid of dimensional analysis, can be used to evaluate rate constants from experimental data. The electroreduction of uranium(VI) to uranium(V) with subsequent second-order disproportionation of uranium(V) has been studied as an experimental test of the model. Disproportionation rate constants thus obtained are in satisfactory agreement with previously reported values. Other possible applications of the model are discussed.**

CHRONOPOTENTIOMETRY with current reversal, first developed by Berzins and Delahay (*1*), has proved useful for investigating electrode processes accompanied by kinetic complications. Testa and Reinmuth (*9*) and Dračka (*3*) have solved the equation for the case where the electrode product undergoes a homogeneous first-order reaction. When higher order kinetics are involved, however, the resulting differential equations are unsolvable.

This paper describes a model of a system in which the electrode process is followed by a homogeneous second-order reaction. The model was tested experimentally by studying the electroreduction of uranium(VI) at a mercury pool electrode; the electrode product, uranium(V), disproportionates to uranium(VI) and uranium(IV).

The model is a large array of numbers representing the concentration of the electroactive species as a function of the distance from the electrode surface. For a given unit of time the mathematical operations corresponding to current passage, diffusion according to Fick's law, and chemical reaction are applied sequentially. These operations are repeated for successive units of time until a certain predetermined condition is achieved—i.e., the concentration of the electroactive reactant becomes zero at the electrode surface. If enough time units are involved, this digital approach is a good approximation to a true continuum. The large number of calculations involved are programmed in Fortran language for the IBM 7094 computer. A working curve relating the forward and reverse transition times to the disproportionation rate constant is thus obtained.

Theory of Model. For a given species there is a series of numbers:

$$C_1, C_2, C_3, C_4 \ldots . C_n$$

where C_1 represents the concentration of that species in unit volume element 1, between zero and one unit distance from the electrode surface; C_2, the concentration in unit volume element 2 (between one and two units distance); C_3, in unit volume element 3, etc.

When a constant flux, I_m (corresponding to a constant current), is applied for a single time unit, the change in concentration in volume element 1 is the net number of units of a given species introduced or removed from the volume element by the electrode process and by diffusion. This may be expressed by the difference equation where the sign

$$\Delta C_1 = \pm I_m + D_m(C_2 - C_1) \qquad (1)$$

of I_m indicates whether the species is being formed or removed at the electrode surface, $(C_2 - C_1)$ represents the concentration gradient, and D_m denotes the diffusion coefficient of the species.

Similarly, ΔC_i for unit volume element $i>1$ is given by

$$\begin{aligned} \Delta C_i = D_m(C_{i+1} - C_i) - \\ D_m(C_i - C_{i-1}) = \\ D_m(C_{i+1} - 2C_i + C_{i-1}) \end{aligned} \qquad (2)$$

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which is a representation of Fick's second law

$$\frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial x^2}$$

Simple Current Reversal Chronopotentiometry Without Kinetic Complications. To test the validity of the method, the model representing simple diffusion controlled current reversal chronopotentiometry was analyzed, and the results were compared to the known theoretical solutions.

Consider the reaction

$$A \overset{e^-}{\rightleftarrows} B \qquad \text{(I)}$$

where both A and B are soluble and have equal diffusion coefficients (adjustments for the inequality of diffusion coefficients are easily made). Let C_m represent the bulk concentration of A. Species B is initially absent from the solution. Thus the initial conditions are:

$$C_m = A_1 = A_2 = A_3 = A_4 = \ldots A_n \qquad (3)$$

$$0 = B_1 = B_2 = B_3 = B_4 = \ldots B_n \qquad (4)$$

The concentration changes for a unit time may be calculated for any unit volume:

$$A_1' = A_1 + \Delta A_1 \quad B_1' = B_1 + \Delta B_1$$
$$A_i' = A_i + \Delta A_i \quad B_i' = B_i + \Delta B_i \qquad (5)$$

Combining Equations 1 and 5 gives

$$A_i' = A_1 - I_m + D_m(A_2 - A_1) \text{ and}$$
$$B_1' = B_1 + I_m + D_m(B_2 - B_1) \qquad (6)$$

Similarly combining Equations 2 and 5, gives

$$A_i' = A_i + D_m(A_{i+1} - 2A_i + A_{i-1}) \text{ and}$$
$$B_i' = B_i + D_m(B_{i+1} - 2B_i + B_{i-1}) \qquad (7)$$

The primed values are calculated for successive i values until $(A_i' - A_i)$ is zero or some predetermined small value. The concentrations are then reset equal to the appropriate primed values. The resulting array represents the concentration profile after the passage of flux I_m for one time unit. The entire process is then repeated, each successive repetition corresponding to the passage of another time unit. These repetitions are continued until $A_1 = 0$. The number of time units required represents the forward transition time, τ_{mf}. Current reversal is achieved by changing the sign of I_m, and continuing the operations as before until $B_1 = 0$. The number of time units required for these operations represents the reverse transition time, τ_{mr}. These operations were programmed for the computer using optimum parametric values. For example, the values

$$C_m = 7 \times 10^5$$
$$I_m = 5 \times 10^3$$
$$D_m = 0.49^1$$

yielded the transition times

$$\tau_{mf} = 7656$$
$$\tau_{mr} = 2594$$
$$\tau_{mr}/\tau_{mf} = 0.339$$

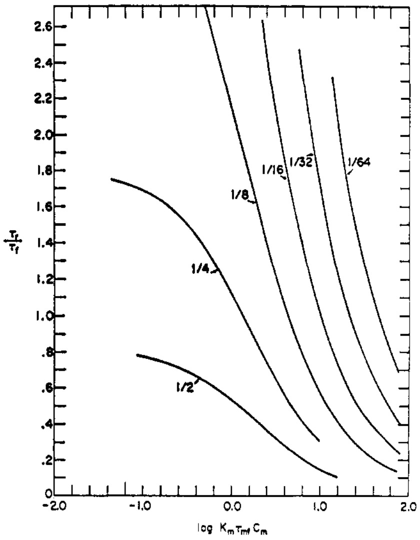

Figure 1. Working curves for current reversal chronopotentiometry. Number on each curve denotes the ratio I_{rm}/I_{fm}

The theoretical τ_{mf} may be calculated from the Sand equation:

$$\tau_{mf} = \frac{\pi D_m C^2}{4 I_m^2} = 7543$$

and the theoretical ratio $\tau_{mr}/\tau_{mf} = 1/3$ (*1*). Thus the errors in τ_{mf} and τ_{mr}/τ_{mf} are about 1% and 2%, respectively. These errors could be reduced by increasing C_m and thereby increasing the transition times, but this would require substantially more computer time than seems warranted.

Current Reversal Chronopotentiometry with Kinetic Complications. When kinetic complications enter in, as in the following scheme:

$$A \overset{e^-}{\rightleftarrows} B$$
$$B \xrightarrow[k_m]{} D \qquad \text{(II)}$$

where species B reacts by some first-order process to give species D and k_m is the first-order rate constant, the kinetics are easily introduced into the model analysis. After having carried out the current and diffusion operations, the value of each unprimed B is reset according to the equation[2]:

$$B_i = B_i' e^{-k_m} \qquad (8)$$

The A values are reset as before.

In an analogous manner one can introduce second-order kinetic complications corresponding to the scheme:

$$A \overset{e^-}{\rightleftarrows} B$$
$$2B \xrightarrow[k_m]{} A + D \qquad \text{(III)}$$

where k_m is the second-order rate constant. Here, the unprimed B values are reset

$$B_i = \frac{B_i'}{B_i k_m + 1} \qquad (9)$$

The A values must also be reset as follows:

$$A_i = A_i' + {}^1/_2 \left[B_i' - \frac{B_i'}{B_i' k_m + 1}\right] =$$
$$A_i' + {}^1/_2 \left[\frac{B_i'^2 k_m}{B_i' k_m + 1}\right] \qquad (10)$$

One experimental difficulty in current reversal chronopotentiometry is the accurate evaluation of very low ratios τ_r/τ_f. When the forward and reverse currents are equal, the ratio has a maximum value of 0.33 and decreases as the kinetic effects become more significant. This problem may be eliminated by reducing the magnitude of the current upon reversal. The ratio of the reverse to forward currents, I_{mr}/I_{mf}, is optimum when the resulting τ_{mr}/τ_{mf} ratio is about unity. Thus, for a given set of model parameters, C_m, D_m, K_m, I_{mf}, a τ_{mr}/τ_{mf} ratio was obtained for each of several values of I_{mr} (see below).

Dimensional Analysis of Model and Development of Working Curve. One may consider a model chronopotentiogram with given parameters to be truly representative of an experimental chronopotentiogram only if (1) the kinetic scheme programmed into the model is representative of the kinetics of the experimental system, and (2) if $I_{mr}/I_{mf} = i_r/i_f$ and $\tau_{mr}/\tau_{mf} = \tau_r/\tau_f$. The experimental quantities are those without the subscript m. It is necessary to convert the model parameters to numbers with units of physical significance. This is easily done if artificial units are assigned to the model. Let the distance unit be L; the species unit, N; and the time unit, T. The parameters written with their units are:

$$C_m(NL^{-3})$$
$$k_m(L^3N^{-1}T^{-1})$$
$$\tau_{mf}(T)$$

---

[1] Examination of the difference equations shows that $D_m = 0.49$ is the maximum value that can be used. A value of $D_m > 0.5$ implies that diffusion could oppose the concentration gradient in violation of Fick's law.

[2] k_m, in the exponential term, really represents the time-rate constant product for one unit time.

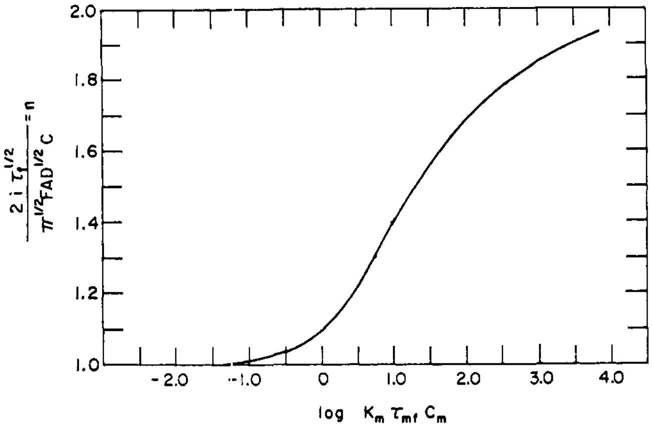

Figure 2. Working curve for conventional chronopotentiometry

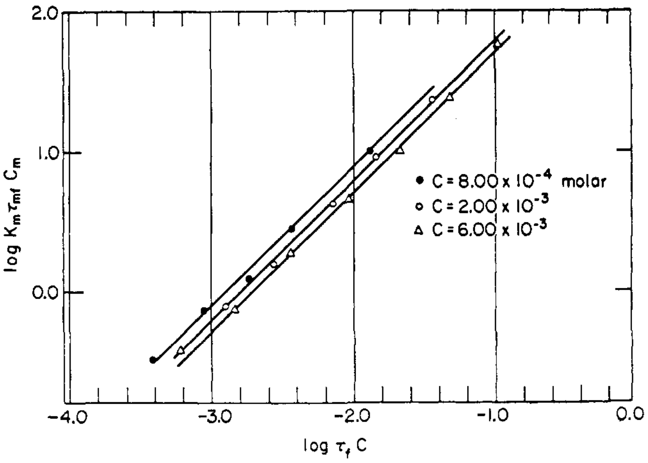

Figure 3. Kinetic data for the disproportionation of uranium (V)

Specified concentrations of U(VI) in 2.97M NaClO$_4$, 0.48M HClO$_4$; 25° C

If the model represents an experimental system, according to the above two criteria, then the following equations may be written relating the model parameters to the experimental parameters:

$$C_m\ (NL^{-3}) = C\ (\text{moles liter}^{-1})$$
$$k_m(L^3N^{-1}T^{-1}) = k\ (\text{liter mole}^{-1}\text{sec.}^{-1})$$
$$\tau_{mf}(T) = \tau_f(\text{sec.})$$
$$\tau_{mr}(T) = \tau_r(\text{sec.})$$

Thus, one can convert the model dimensions to real units:

$$k_m\ \frac{C_m}{C}\ \frac{\tau_{mf}}{\tau_f}\ (\text{liter mole}^{-1}\text{sec.}^{-1}) = k\ (\text{liter mole}^{-1}\text{sec.}^{-1}) \quad (11)$$

Separating the experimental and model parameter gives an equation relating dimensionless quantities:

$$k_m C_m \tau_{mf} = kC\tau_f \quad (12)$$

Similarly one can obtain:

$$\frac{2I_m\tau_{mf}^{1/2}}{\pi^{1/2}D_m^{1/2}C_m} = \frac{2i\tau_f^{1/2}}{\pi^{1/2}FD^{1/2}C} \quad (13)$$

Because Equations 12 and 13 relate dimensionless quantities, plots (semilog, to expand the range) of

$\frac{\tau_{mf}}{\tau_{mf}}$ vs. log $k_m\tau_{mf}C_m$ (for current reversal chronopotentiometry)

or $(2I_m\tau_{mf}^{1/2})/(\pi^{1/2}D_m^{1/2}C_m)$ vs. log $k_m\tau_{mf}C_m$ (for conventional chronopotentiometry) will provide working curves for evaluating the rate constant from experimental data (Figures 1, 2). The current reversal relationship is the easier one to use since it does not involve the electrode area. The curves in Figure 1 correspond to several values of I_{mr}/I_{mf}—i.e., $^1/_2$, $^1/_4$, $^1/_8$, $^1/_{16}$, $^1/_{32}$, and $^1/_{64}$. It is clear from Figure 1 that transition time ratios of about unity can be obtained only if the ratio $I_{mr}/I_{mf} < {}^1/_4$. Testa and Reinmuth (*9*) have rigorously derived the analogous relationship for first-order kinetics (Scheme II), the working curve in this case being:

$$\frac{\tau_r}{\tau_f}\ vs.\ k\tau_f$$

This relationship follows directly from the equation relating the following dimensionless quantities:

$$k_m\tau_{mf} = k\tau_f$$

Application of Theory to Studies of Disproportionation of Uranium(V). The reduction of uranium(VI) to uranium(V) at a mercury electrode and the subsequent disproportionation of this species proceed according to Scheme III in acid medium. Several workers have studied this system and shown that the disproportionation is second order in uranium(V) and first order in hydrogen ion (*4–8*). The following mechanism has been proposed:

i. $UO_2^{+2} \overset{e^-}{\rightleftarrows} UO_2^+$

ii. $UO_2^+ + H^+ \overset{K}{\rightleftarrows} UOOH^{+2}$
(equilibrium lies mostly to the left)

iii. $UO_2^+ + UOOH^{+2} \xrightarrow{k}$
$UO_2^{+2} + UOOH^+$
$H^+ + UOOH^+ \xrightarrow{\text{fast}} UO^{+2} + H_2O$

The kinetics were investigated at several concentrations of UO_2^{+2} while the hydrogen ion activity was held constant in a high ionic strength supporting electrolyte.

Table I. Chronopotentiometry of U(VI) in 2.97*M* NaClO$_4$–0.48*M* HClO$_4$; *T* = 25° C.

Concn. uranium (VI) (*M*)	i_f, amp.	i_r, amp.	$\frac{i_r}{i_f}$	τ_f, sec.	$\frac{\tau_r}{\tau_f}$	log $\tau_f C$
8.00×10^{-4}	1.20×10^{-4}	1.50×10^{-5}	$^1/_8$	16.5	0.585	−1.84
	2.00×10^{-4}	2.50×10^{-5}	$^1/_8$	4.66	1.31	−2.39
	2.80×10^{-4}	7.00×10^{-5}	$^1/_4$	2.32	1.03	−2.69
	4.00×10^{-4}	1.00×10^{-4}	$^1/_4$	1.12	1.24	−3.01
	6.00×10^{-4}	1.50×10^{-4}	$^1/_4$	0.48	1.49	−3.38
2.00×10^{-3}	3.00×10^{-4}	1.87×10^{-5}	$^1/_{16}$	19.0	0.555	−1.40
	4.50×10^{-4}	2.81×10^{-5}	$^1/_{16}$	7.25	1.08	−1.80
	6.00×10^{-4}	7.50×10^{-5}	$^1/_8$	3.79	1.02	−2.52
	9.00×10^{-4}	2.25×10^{-4}	$^1/_4$	1.43	0.93	−2.52
	1.30×10^{-3}	3.25×10^{-4}	$^1/_4$	0.633	1.21	−2.86
	1.90×10^{-3}	4.75×10^{-4}	$^1/_4$	0.293	1.41	−3.21
6.00×10^{-3}	1.00×10^{-3}	1.5625×10^{-5}	$^1/_{64}$	17.2	0.870	−0.95
	1.40×10^{-3}	4.37×10^{-5}	$^1/_{32}$	7.92	0.935	−1.28
	2.00×10^{-3}	1.25×10^{-5}	$^1/_{16}$	3.60	1.00	−1.63
	2.80×10^{-3}	3.50×10^{-4}	$^1/_8$	1.54	0.985	−2.00
	4.00×10^{-3}	1.00×10^{-3}	$^1/_4$	0.607	0.86	−2.40
	6.00×10^{-3}	1.50×10^{-3}	$^1/_4$	0.241	1.22	−2.80
	9.00×10^{-3}	2.25×10^{-3}	$^1/_4$	0.101	1.45	−3.18

EXPERIMENTAL

Reagents. Uranium perchlorate stock solution was prepared by dissolving uranium trioxide powder in perchloric acid (Baker A.R.). The solution was neutralized with sodium carbonate (Baker A.R.) until only a slight excess of acid remained. The uranium(VI) concentration was 1.00 × $10^{-1}M$, determined by controlled potential coulometry. The supporting electrolyte solution containing $2.97M$ sodium perchlorate and $0.48M$ perchloric acid (ionic strength 3.45) was prepared by neutralizing perchloric acid with sodium carbonate.

All solutions were prepared with triply distilled water.

The working electrode consisted of triply distilled mercury which had been washed in dilute perchloric acid and rinsed thoroughly with distilled water.

Table II. Effect of Concentration of Uranium(IV) on the Disproportionation Rate Constant

Concn. U(VI) (M)	k (l. mole^{-1} sec.$^{-1}$)	k/C_{H^+}
6.00 × 10^{-3}	5.0 × 10^2	1.04 × 10^3
2.00 × 10^{-3}	6.3 × 10^2	1.31 × 10^3
8.00 × 10^{-4}	7.6 × 10^2	1.58 × 10^3

Table III. Fortran Program Data

```
          DIMENSIφNX(3,999),Y(3,999),XX(3,999)
     100  READINPUTTAPE5,16,D,Z,ZZ,R,RX,W,RT,C,L,JA,JB,II
      16  FφRMAT(6F6.4,E8.0,F8.0,4I4)
          WRITEφUTPUTTAPE6,317
     317  FφRMAT(42H INPUT DATA D,Z,ZZ,R,RX,W,RT,C,L,JA,JB,II)
          WRITEφUTPUTTAPE6,316,D,Z,ZZ,R,RX,W,RT,C,L,JA,JB,II
     316  FORMAT(1H 6F10.4,E20.8,F12.0,4I8)
          Zφ=Z
          ML=0
          N=0
          M=0
          Dφ101=1,999
          X(2,I)=0
          X(1,I)=0
     101  X(3,I)=0
     111  RZ=Z/Zφ
          WRITEφUTPUTTAPE6,321,Zφ,Z,RZ
     321  FφRMAT(1H 3F20.8)
       1  N=N+1
          M=M+1
          IF(X(ML+1,1))8,8,2
       2  Y(1,1)=X(1,1)-Z+D*(X(1,2)-X(1,1))
          Y(2,1)=X(2,1)+Z+D*(X(2,2)-X(2,1))
          Y(3,1)=X(3,1)+D*(X(3,2)-X(3,1))
          Dφ3I=2,998
          IK=I
          Dφ13J=1,3
      13  Y(J,I)=X(J,I)+D*(X(J,I+1)-2.0*X(J,I)+X(J,I-1))
          IF(I-5)3,6,6
       6  IF(ML)17,17,86
      17  IF(C-Y(1,I)-W*(C-Y(1,1)))4,4,3
      86  IF(Y(2,I)-W*C)4,4,3
       3  CφNTINUE
       4  Dφ61I=1,IK
          X(2,I)=Y(2,I)/(ABSF(RT*Y(2,I)+1.0)
kinetics  DELC=(Y(2,I)-X(2,I))/2.0
          X(1,I)=Y(1,I)+DELC
      61  X(3,I)=Y(3,I)+DELC
          IF(N-L)1,7,7
       7  N=0
       8  WRITEφUTPUTTAPE6,25,M,((X(JJ,K),JJ=1,3),K=1,JA,JB)
      25  FφRMAT(1HOI5/(6X,3E20.8))
          IF(N)1,1,9
       9  IF(ML)99,99,199
      99  MI=M
          Z=-Z*R
          Dφ81I=1,999
          Dφ82J=1,3
      82  XX(J,I)=X(J,I)
      81  CφNTINUE
          GφTφ 603
     199  Z=Z*RX
          IF(II)31,31,32
      31  IF( 2-M- 3*MI)30,30,100
      32  IF(ABSF(Z))-ZZ)100,30,30
      30  Dφ601I=1,999
          Dφ602J=1,3
     602  X(J,I)=XX(J,I)
     601  CφNTINUE
     603  M=0
          N=0
          ML=1
          GφTφ 111
```

Instrumentation. Two electronically regulated constant current supplies were used to provide individually controlled forward and reverse current densities. The currents were continually checked by noting the potential across a precision resistor with a Rubicon potentiometer. A Philbrick P-2 operational amplifier was used as a voltage follower. Electronic equipment detected the potential break at the forward transition time and reversed the current automatically, by means of a Stevens-Arnold Millisec relay (response time ~0.5 msec.). The chronopotentiograms were recorded with a Dumont Oscillograph Record Camera (using Polaroid film 3000 type 47) and a Tektronix 502 Oscilloscope. A precision sine-square wave generator, Model E-310, was used to calibrate the oscilloscope at fast sweep rates.

Cell. The cell is a modification of the one described by Delahay (*2*) for chronopotentiometry with a mercury pool. The cup and cell top were made of Teflon; the area of the pool was 2.0 sq. cm. A platinum wire coil served as the reference electrode and attained a steady potential of about +0.4 volt *vs.* SCE in the test solution. This electrode was used instead of the more conventional reference electrodes to avoid introducing foreign ions into the electrolyte. The electrode was contained in a fritted side compartment and contact with the mercury pool was made through a Luggin capillary. A platinum wire coil was used as the auxiliary electrode.

A constant temperature bath maintained the cell temperature at 25° ± 0.1° C.

RESULTS

A series of chronopotentiograms with current reversal was obtained for each of three concentrations of uranium (VI) (6.00 × $10^{-3}M$, 2.00 × $10^{-3}M$, and 8.00 × $10^{-4}M$). For each chronopotentiogram the ratio i_r/i_f was adjusted to values $^1/_4$, $^1/_8$, $^1/_{16}$, $^1/_{32}$, or $^1/_{64}$ so that the ratio τ_r/τ_f was approximately unity. Experimental data are summarized in Table I.

From the ratio τ_r/τ_f, one can obtain the corresponding term log $k_m\tau_mC_m$, using the appropriate working curve (Figure 1). Taking the logarithm of both sides of Equation 12 gives:

$$\log k_m\tau_{mf}C_m = \log k + \log(\tau_fC)$$

Thus a plot of log $k_m\tau_{mf}C_m$ *vs.* log (τ_fC) gives a straight line with a slope of unity (Figure 3), and the rate constant may be evaluated from the intercept (log $k_m\tau_{mf}C_m = 0$):log $k = -\log(\tau_fC)$. Values of k corresponding to the three concentrations investigated are shown in Table II.

Table IV. Input Data

Computer symbol	Definition	Value
D	Diffusion coefficient	0.4900
Z	Flux prior to reversal	5000.0
RT	Rate constant	4.0×10^{-8}
C	Bulk concentration of species A	250000.
R	Current ratio control (statement following 99)	1.00
RX	Current ratio control (statement 199)	0.5000
II	Program control (statement following 199)	0
ZZ	Program control (statement 32) is nonoperating unless II > 0	0
W	Program control (statements 17, 86)	0.0001
L	Readout control (statement following 61)	100
JA	Readout control (statement 8)	1
JB	Readout control (statement 8)	1

Table V. Output Data for Input Listed in Table IV

$\frac{I_{mr}}{I_{mf}}$	τ_{mf}	τ_{mr}	$\frac{\tau_{mr}}{\tau_{mf}}$	$k_m\tau_{mf}C$	log $k_m\tau_{mf}C$
1.000	2296	87	3.8×10^{-2}	23.0	1.35
0.500		192	8.4×10^{-2}		
0.250		389	1.69×10^{-1}		
0.125		731	3.18×10^{-1}		
0.0625		1298	5.61×10^{-1}		
0.03125		2214	9.64×10^{-1}		
0.015625		3672	1.60		

Agreement with theory is excellent for a given uranium (VI) concentration, but there is an as yet unexplained systematic variation of k with concentration. The k value for the highest concentration, when normalized to unit [H^+], is close to the value 0.95×10^3 liter mole^{-1} sec.$^{-1}$ obtained polarographically by Orlemann and Kern (*8*). The same authors, however, obtained a value twice as high when using a more direct method. The suggested mechanism is inadequate.

Range of Method. The uranium system was chosen as an illustrative example. One can study analogous systems obeying the same kinetic scheme, with second-order rate constants ranging from 1 to 10^5 liter mole^{-1} sec.$^{-1}$ It should be noted that one measurement of τ_f and τ_r is sufficient to estimate the rate constant.

Applicability of Model. The model described in this paper is applicable to similar problems involving complex kinetics which cannot be treated by rigorous mathematical analysis. The model is not limited to chronopotentiometry; analogous models for potentiostatic studies can be easily developed.

Using the model, one can calculate concentration profiles of all species involved in a given system, at all times of interest. This could provide information as to the kind of approximation which can be validly made to achieve a mathematical solution.

IBM 7094 FORTRAN PROGRAM

The Fortran program describes the calculation of the forward and reverse transition times for a given chemical system. The bracketed portion of the program, which describes the calculation of the kinetic effects (Scheme III), can be easily modified for different kinetic mechanisms.

Doubly subscripted variables X, Y, and XX are used, the first subscript having a value of 1, 2, or 3, and corresponding to species A, B, or D, respectively, in Scheme III. The second subscript, having values 1 to 999, denotes "distance" from the electrode surface.

Table IV shows a sample set of input data. The resulting output data are shown in Table V.

The "concentration profiles" of the three species at various times of calculation (see "Readout control" L, JA, JB, in Table IV) are not listed.

The total computing time for Table V is about 11 minutes. This time will depend, of course, upon the transition time (τ_{mf} should be greater than 2000 to minimize error) and upon the quantity of information desired in the readout.

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