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Cyclic Chronopotentiometry. Determination of Types and Rates of Second Order Chemical Reactions Following Electron Transfer*

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Cyclic chronopotentiometry, a convenient technique for studying coupled chemical and electrochemical reaction mechanisms, is extended to include determination of types and rates of second order chemical reactions following electron transfer. The mathematical treatment presented is derived on the basis of Feldberg's method of digital simulation. Diagnostic curves are given for kinetic and disproportionation reactions. The disproportionation reaction of uranium(V) in carbonate solutions has been used for an experimental test. The technique and the described method of calculation of data allow determination of the rate coefficient of a second order disproportionation reaction to within ± 2% of a typical value of 10 l mole^{-1} sec^{-1}. The technique of cyclic chronopotentiometry is applicable for second order rate coefficients between 10^{-1} and 10^5 l mole^{-1} sec^{-1}.

INTRODUCTION

Cyclic chronopotentiometry (CCP) is a method of electrolysis with constant current which is successively reversed each time the potential of the working electrode reaches certain, predetermined, upper and lower levels. The method has been devised and defined in these terms by Herman and Bard[1], who were also the first to apply this method to the study of complex electrochemical reaction mechanisms.[2-4]

The result of a CCP experiment is a series of transition times characteristic for each of many possible reaction mechanisms. Herman and Bard[1] have also introduced the presentation of data obtained in dimensionless units, a_N vs. N, where $a_N = \tau_N/\tau_1$, with τ_N and τ_1 being the transition time of the N-th and the first cycle, respectively.

Complex reaction mechanisms are quite common in ionic oxidation — reduction processes in complexing media. Delahay[5] has shown that some metal complexes have to rearrange or dissociate prior to electron transfer. There are many examples of complex reaction mechanisms in organic systems[6],

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and the elucidation of some has proved so far of considerable value for applied, preparative work.

There are several electrochemical experimental techniques which offer insight into the mechanism of coupled chemical and electrochemical reactions. Among these special mention deserve polarography[7], the rotating ring-disc electrode[8], voltammetry[9], single pulse chronopotentiometry (CP)[10] and current reversal chronopotentiometry (CRCP)[11,12].

A certain experimental method is the more useful the less the final result depends on data which have to be determined independently. In addition, its relative merits are judged on the basis of the amount of information obtainable from a single experiment. The advantages are in elimination of environmental influence, noise errors, and operator's mistakes.

Polarography, applied to complex kinetics requires independent measurement of the drop time and current. The rate of revolution and the gap between electrodes has to be known in the ring-disc electrode technique. Determination of the electrode surface area and consequently of the current density is a prerequisite in CP.

The CRCP and the CCP techniques yield dimensionless parameters from which the rate coefficients can be determined. The advantage of CCP over CRCP is in the fact that a single experiment is capable of revealing the type of the coupled mechanism and also is giving a sufficient number of data for statistical analysis.

Herman and Bard[4] have shown that a CCP experiment will give information on the type of any first order chemical reaction preceding, following, or both, electron transfer. Fitting of a calculated a_N *vs.* N curve to experimental data will give discrete values for the rate coefficients, k_f and k_b. In contrast, a CP experiment would yield only the function $\phi = K(k_f + k_b)^{1/2}$ for a preceding chemical reaction. Independent knowledge of the equilibrium constant, K, is necessary to calculate the k's.

The present work aims to show that a single CCP experiment provides information on the type of coupled second order chemical transformation. Rate coefficients, k_f and k_b, can be estimated from the same experiment by numerical fitting requiring only a moderate computation effort.

MATHEMATICAL TREATMENT

The treatment used in this work is an extension from CRCP to CCP of the digital simulation technique used by Feldberg and Auerbach[13] and by Feldberg[14]. Essentially, this is the method of finite differences, an approach often used in treating second order differential equations for which no analytical solutions are readily available. It has been successfully applied also to chronoamperometry[15], linear scan[16] and cyclic voltammetry[17]. The three types of frequently observed second order chemical reactions, following electron transfer, are described in Table I.

The computer program, written in Fortran II is given in the Appendix. It has been generated following the ideas of Feldberg[14]. The idealized model of the diffusion layer is divided into compartments, with the surface itself taken as the zero-th. Next, a sequence of identical constant current pulses is applied. Each pulse represents a time unity. Passage of current produces changes in concentration. Part of this concentration loss is counteracted by

TABLE I

Various Types of Second Order Chemical Reactions Following Electron Transfer

Mechanism		Kinetic equations
type	chemical equations	
catalytic	$O + e \longrightarrow R$ $R + Y \xrightarrow{k} O + Z$	$\frac{\delta C_O}{\delta t} = D_O \frac{\delta^2 C_O}{\delta x^2} + kC_R C_Y$ $\frac{\delta C_R}{\delta t} = D_R \frac{\delta^2 C_R}{\delta x^2} - kC_R C_Y$
kinetic (dimerization)	$O + e \longrightarrow R$ $2R \xrightarrow{k} Z$	$\frac{\delta C_O}{\delta t} = D_O \frac{\delta^2 C_O}{\delta x^2}$ $\frac{\delta C_R}{\delta t} = D_R \frac{\delta^2 C_R}{\delta x^2} - 2kC_R^2$
disproportionation	$O + e \longrightarrow R$ $2R \xrightarrow{k} O + Z$	$\frac{\delta C_O}{\delta t} = D_O \frac{\delta^2 C_O}{\delta x^2} + kC_R^2$ $\frac{\delta C_R}{\delta t} = D_R \frac{\delta^2 C_R}{\delta x^2} - 2kC_R^2$

diffusion. In the next step this concentration is modified by the chemical transformation of the product. A certain number of pulses produces zero concentration of the initially present electroactive species at the electrode surface. This number is the first transition time. Now, the current is reversed and the treatment repeated, mutatis mutandis, until the concentration of the product of the first electrode reaction reaches zero at the surface of the electrode. On obtaining the second transition time, the current is again reversed. As a limit 20 transition times have been calculated (10 forward, or *odd cycles* and 10 back, or *even cycles*). The program is written to yield $\tau_{m,N}$ and $a_{m,N}$ values for a certain typical model rate coefficient, k_m. C_m is the model concentration of the electroactive species. For a close fitting of a model to an experimental a_N *vs.* N curve, Feldberg's correlation postulate

$$k_m C_m \tau_{m,N} = kC\tau_N$$

is valid. Knowing the experimental concentration of the electroactive species and the N-th relative transition time, the rate coefficient, k, of the second order irreversible reaction can be calculated. Actually, a number of k values, one for each N, is obtained, and some measure of the dispersion of data is the result.

Validity of the program, given in Appendix, has been tested. After changing the DO 13 loop, the program was run to simulate a first order kinetic model, the same as given by Herman and Bard[4]. Table II shows the results. The maximum relative deviation is 0.22%, an order of magnitude less than the expected precision of an experimental transition time determination.

TABLE II

Relative Transition Times, a_N, for First Order Following Chemical Reaction, Calculated by Two Different Methods

$I_f = 2\ I_b,\ D_O = D_R$

No. of cycles N	1	2	Difference (2)—(1)	Relative Deviation %
	$k\tau_1 = 0.32724$	k = 0.001 TAU 1 = 327.24		
1	1.00000	1.00000	—	—
2	0.57338	0.57343	0.00005	0.01
3	0.58179	0.58181	0.00002	0.00
4	0.52693	0.52720	0.00027	0.05
5	0.48382	0.48396	0.00014	0.03
6	0.48176	0.48212	0.00036	0.07
7	0.42319	0.42339	0.00020	0.05
8	0.44482	0.44539	0.00057	0.13
9	0.38014	0.38042	0.00028	0.07
10	0.41473	0.41538	0.00065	0.16
11	0.34741	0.34779	0.00038	0.11
12	0.38991	0.39078	0.00087	0.22
13	0.32149	0.32198	0.00049	0.15
14	0.36902	0.36976	0.00074	0.20
15	0.30031	0.30075	0.00044	0.15
16	0.35118	0.35181	0.00063	0.18
17	0.28261	0.28300	0.00039	0.14
18	0.33575	0.33640	0.00065	0.19
19	0.26755	0.26794	0.00039	0.15
20	0.32224	0.32295	0.00071	0.22

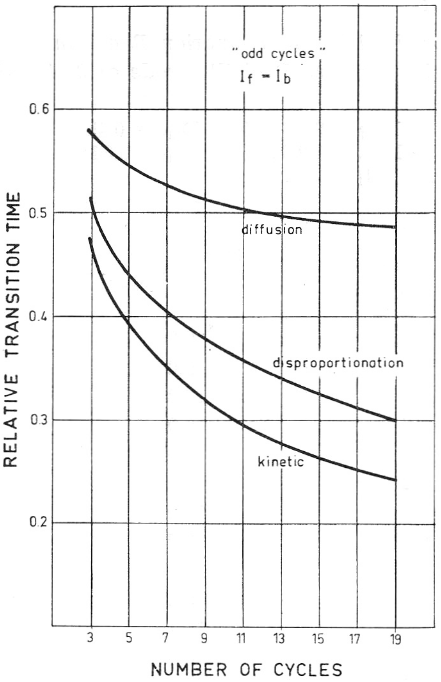
Column 1: Numerical solution of differential equations. After Herman and Bard[3].
Column 2: Digital simulation. Program given in Appendix, with changes in the DO 13 loop for first order chemical reaction.

Figs. 1. and 2. show the general form of the a_N *vs.* N curves for a case with no chemical complications, and for two types of second order following chemical reactions, for odd and even cycles, respectively. The curves clearly indicate differences in the mechanisms. Amplification of these differences with increasing number of cycles represents also an advantage of CCP over CP or CRCP.

EXPERIMENTAL TEST

The disproportionation reaction of uranium(V) in carbonate solution has been used as a test model. Fig. 3. has been obtained for a 1m*M* solution of uranium(VI) in 1*M* $NaHCO_3$, *p*H = 8.5. Good fit with the calculated a_N *vs.* N curve for second order disproportionation mechanism is obtained.

Calculated data of this experiment are tabulated in Table III. Further data with detailed discussion will be reported on in a subsequent paper.



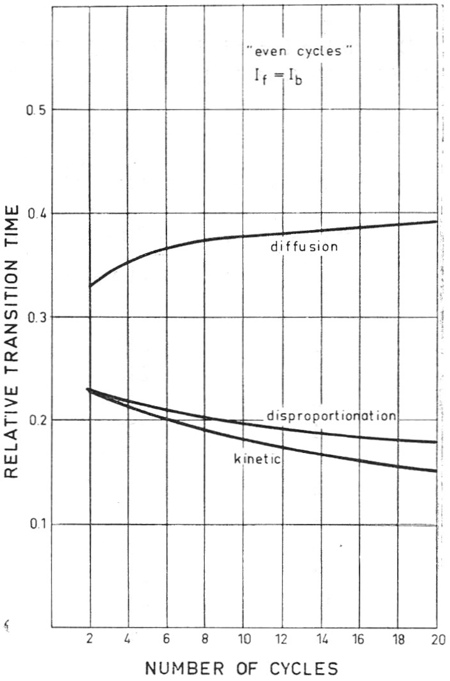


Fig. 1. Relative transition times *vs.* number of cycles in the forward direction *(odd cycles)* for an electrochemical reaction with no chemical complications (diffusion), and for a following disproportionation and for kinetic chemical reactions. The electrolysis current is the same in the forward and the back direction. The two lower curves have been obtained by the method of digital simulation.

Fig. 2. The same as Fig. 1 except for the electrochemical reaction in the back direction *(even cycles)*. Note differences in the two lower curves beginning with 4th cycle.

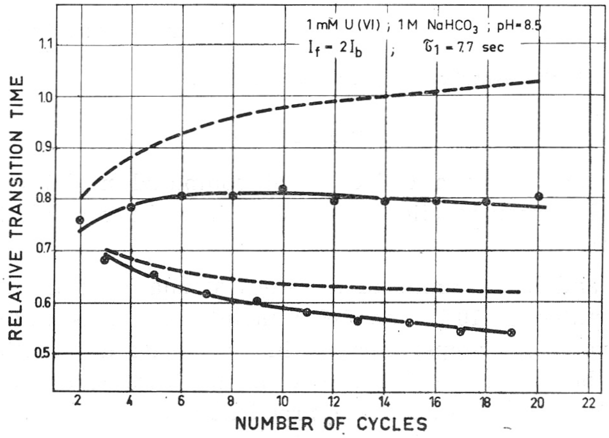


Fig. 3. The relative transition time *vs.* number of cycles for the electrolysis of uranium(VI) in $NaHCO_3$. The circles are experimental data, the full line represents calculated values for a disproportionation mechanism with input data from Table III. The dashed line shows calculated data for pure diffusion control.

TABLE III

Determination of the Rate Coefficient for the Disproportionation Reactic of Uranium(V) in 1 M *$NaHCO_3$, pH = 8.5, at the Mercury Pool Electrode of 3.*

Model values input data: $C_m = 1.0$ $I_{m,f} = 2.6 \times 10^{-2}$ $D_{m6} = 0.45$
$k_m = 1.4 \times 10^{-4}$ $I_{m,b} = 1.3 \times 10^{-2}$ $D_{m5} = 0.34$*
Experimental input data: $C = 1.0$ mM $I_f = 2 I_b$

No. of cycles N	Transition time		Rate Coefficient k [l mole^{-1} sec^{-1}]
	Model value $\tau_{m,N}$	Experimental τ [sec]	
1	542.0	7.7	9.9
2	398.3	5.8	9.6
3	372.4	5.2	10.0
4	427.3	6.0	10.0
5	348.4	5.0	9.8
6	436.3	6.2	9.9
7	334.7	4.7	10.0
8	439.0	6.2	9.9
9	324.8	4.6	9.9
10	438.8	6.3	9.8
11	316.9	4.4	10.1
12	437.3	6.1	10.0
13	310.3	4.3	10.1
14	434.9	6.1	10.0
15	304.5	4.3	9.9
16	432.0	6.1	9.9
17	299.3	4.1	10.2
18	428.9	6.1	9.8
19	294.5	4.1	10.0
20	425.7	6.2	9.6
			Mean value: 9.9 ± 0.15

* The D_{m6}/D_{m5} ratio is the experimentally observed value[18].

RESULTS

Tables IV and V are a collection of computed model data apr to the disproportionation reaction of uranium in carbonate solution of pH and ionic strength.

The upper and lower limits of k values amenable to treatment b have been estimated at 10^{-1} and 10^5 l mole^{-1} sec^{-1}. This estimate is on a current ratio (I_f, amps: current in the *forward* direction; I_b, current in the *back*, direction) $I_f/I_b = 4$ at the lower limit, and I_f/I at the upper one. These are the best practicable values in CCP expe designed either to distinguish between disproportionation and charge t without chemical complications, or to measure the rate coefficient of reaction with optimum precision.

TABLE IV

Calculated Transition Times and Relative Transition Times $\tau_{m,N}/\ _{m,1} = a_{m,N}$ *for a Disproportionation Reaction*

Input data: $C_m = 1.0$
$D_{m6} = 0.45$
$D_{m5} = 0.34$
$I_{m,f} = 2.6 \times 10^{-2}$
$I_{m,b} = 1.3 \times 10^{-2}$

	$k_m = 1.4 \times 10^{-4}$		$k_m = 5.5 \times 10^{-4}$	
N	$\tau_{m,N}$	$a_{m,N}$	$\tau_{m,N}$	$a_{m,N}$
1	542.0	1.000	601.9	1.000
2	398.3	0.735	347.4	0.577
3	372.4	0.687	381.9	0.634
4	427.3	0.788	347.7	0.578
5	348.4	0.643	340.6	0.566
6	436.4	0.805	340.0	0.565
7	334.7	0.617	315.4	0.524
8	439.0	0.810	331.4	0.551
9	324.8	0.599	296.7	0.493
10	438.9	0.810	323.3	0.537
11	316.9	0.585	282.4	0.469
12	437.3	0.807	315.8	0.523
13	310.3	0.573	270.5	0.449
14	434.9	0.802	309.0	0.513
15	304.5	0.562	260.5	0.433
16	432.0	0.797	302.8	0.503
17	299.3	0.552	251.7	0.418
18	428.9	0.791	297.1	0.493
19	294.5	0.543	244.2	0.405
20	425.7	0.786	291.9	0.485

TABLE V-a

Calculated Transition Times and Relative Transition Times, $\tau_{m,N}/\tau_{m,1} = a_{m,N}$ *for a Disproportionation Reaction following electron transfer*

Input data: $C_m = 1.0$ $D_{m6} = 0.45$ $D_{m5} = 0.34$

	$I_{m,f} = 3.2 \times 10^{-2}$ $I_{m,b} = 0.8 \times 10^{-2}$ $k_m = 6.5 \times 10^{-4}$		$I_{m,f} = 2.6 \times 10^{-2}$ $I_{m,b} = 0.65 \times 10^{-2}$ $k_m = 4.7 \times 10^{-4}$	
N	$\tau_{m,N}$	$a_{m,N}$	$\tau_{m,N}$	$a_{m,N}$
1	385.6	1.000	589.8	1.000
2	504.9	1.309	751.9	1.275
3	282.9	0.734	429.0	0.727
4	525.9	1.364	778.1	1.319
5	259.4	0.672	391.4	0.664
6	521.9	1.354	769.6	1.305

TABLE V-a continued

N	$\tau_{m,N}$	$a_{m,N}$	$\tau_{m,N}$	$a_{m,N}$
7	243.6	0.632	366.4	0.621
8	513.1	1.331	755.0	1.280
9	231.7	0.601	347.6	0.589
10	503.4	1.306	739.7	1.254
11	222.3	0.577	332.6	0.564
12	494.1	1.281	725.2	1.230
13	214.0	0.555	319.9	0.542
14	485.2	1.258	711.6	1.207
15	207.3	0.538	309.3	0.524
16	477.0	1.237	699.1	1.185
17	201.0	0.521	299.7	0.508
18	469.3	1.217	687.5	1.166
19	195.7	0.508	291.5	0.494
20	462.2	1.199	676.8	1.148

TABLE V-b

$I_{m,f} = 3.0 \times 10^{-2}$
$I_{m,b} = 0.75 \times 10^{-2}$

	$k_m = 1.4 \times 10^{-3}$		$k_m = 1.55 \times 10^{-3}$		$k_m = 3.0 \times 10^{-3}$	
N	$\tau_{m,N}$	$a_{m,N}$	$\tau_{m,N}$	$a_{m,N}$	$\tau_{m,N}$	$a_{m,N}$
1	512.7	1.000	523.0	1.000	647.0	1.000
2	461.2	0.900	445.1	0.847	332.5	0.513
3	324.8	0.633	324.0	0.616	305.7	0.473
4	448.9	0.875	430.4	0.818	312.8	0.483
5	279.7	0.545	276.7	0.526	248.7	0.384
6	432.6	0.844	413.9	0.787	299.1	0.462
7	252.7	0.493	248.9	0.473	218.7	0.338
8	418.4	0.816	400.0	0.760	288.8	0.446
9	233.9	0.456	229.8	0.437	198.8	0.307
10	406.4	0.793	388.3	0.738	280.5	0.434
11	219.9	0.429	215.7	0.410	184.7	0.286
12	396.1	0.773	378.3	0.719	273.6	0.423
13	208.7	0.407	204.4	0.389	173.7	0.269
14	387.1	0.755	369.6	0.703	267.6	0.414
15	199.6	0.389	194.8	0.370	164.8	0.255
16	379.1	0.739	361.9	0.688	262.4	0.406
17	191.6	0.374	186.9	0.355	157.6	0.244
18	371.9	0.725	355.1	0.675	257.7	0.398
19	184.8	0.360	180.5	0.343	151.1	0.234
20	365.5	0.713	349.0	0.664	253.5	0.392

APPARATUS

The block diagram of the electronic unit used for CCP is given in Fig. 4. It was built using Analog Devices operational amplifiers. The instrument has two independent constant current generators. These are capable of maintaining the electrolysis current within 0.1% of a value set anywhere between 1×10^{-6} and 3×10^{-2} A. The maximum output voltage is 25 V D. C. P_4 and P_5 are the (critical) upper and lower level preset potentiometers. The discriminators have sensitivities and repeatabilities within ± 1 mV. The switching time is 2 microseconds. The unit has a built-in 10 kHz oscillator-timer, from which impulses are fed into a 20 channel memory device. Details of the electronic circuitry will be given elsewhere[20].

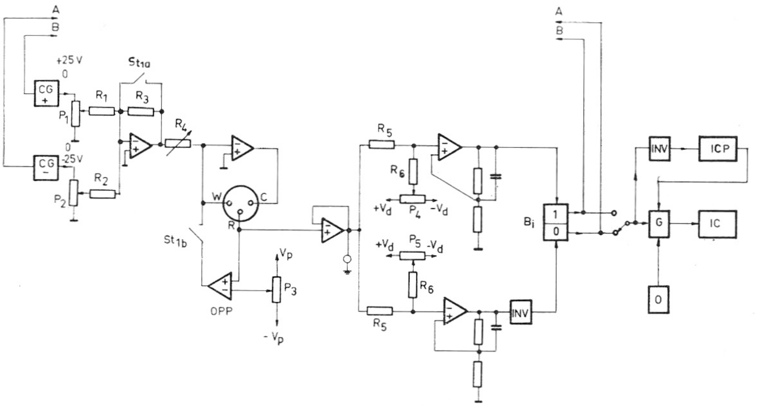


Fig. 4. Block diagram of the electronic instrument for cyclic chronopotentiometry. CG+ and CG— are two independent constant current generators, OPP is the potentiostat to keep the potential of the working electrode at a defined potential prior to chronopotentiometric measurement, P_4 and P_5 are preset potentiometers determining the upper and lower level of critical reversing potentials, Bi is the bistable electronic switching circuit, O is the 10 kHz oscillator, G gate, ICP the cycle preset counter, and IC the impulse counter and memory device.

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APPENDIX

Computer Program in Fortran II for Cyclic Chronopotentiometry. Second order chemical transformation following electron transfer.

The treatment is analogous to that of Feldberg[14].
Input data are:

CM	concentration of electroactive species
ZF, ZB	current in the forward, back, direction
D6, D5	diffusion coefficients of reactant, product
RC	rate coefficient of the chemical reaction
KK	number of cycles

```
C      CYCLIC CHRONOPOTENTIOMETRY,DIMENSIONAL ANALYSIS
C      CHEMICAL REACTION 2ND ORDER,DISPROPORTIONATION
       DIMENSION A[900],B[900],AA[900],BB[900]
       ACCEPT TAPE 1,CM,ZF,ZB.D6,D5,RC,KK,KP
1      FORMAT[6E10.3,2I5]
       PRINT 40,CM,ZF,ZB,D6,D5,RC,KK
40     FORMAT[$CONCN.=$,E10.4,5X,$CURR.F=$,E10.4,
      1//$CURR.B=$,E10.4,5X,$D.COEF6.=$,E10.4,
      2//$D.COEF5.=$,E10.4,5X,$R.C.=$,E10.4,5X,$N.OF CYC.=$,I4]
       SENSE LIGHT 1
       DO 2 I=1,900
       A[I]=CM
       AA[I]=CM
       B[I]=0
2      BB[I]=0
       NMAX=0
53     DO 50 K=KP,KK
       N=0
77     IF[MOD[K,2]]3,4,3
3      PR=-1.
       Z=ZF
       CC=A[1]-[Z/[2*D6]]
       GO TO 5
4      PR=1.
       Z=ZB
       CC=B[1]-[Z/[2*D5]]
5      N=N+1
       NMAX=NMAX+1
       MAXV=6.*SQRT[D6*NMAX]+0.9
7      AA[1]=A[1]+PR*Z+D6*[A[2]-A[1]]
       BB[1]=B[1]-PR*Z+D5*[B[2]-B[1]]
       LM=MAXV-1
       DO 8 I=2,LM
       AA[I]=A[I]+D6*[A[I-1]-2.*A[I]+A[I+1]]
8      BB[I]=B[I]+D5*[B[I-1]-2.*B[I]+B[I+1]]
       IF[CC+0.00001]6,6,74
74     DO 13 I=1,MAXV
       DELTA=-RC*BB[I]*BB[I]
       A[I]=AA[I]-DELTA
13     B[I]=BB[I]+2.0*DELTA
       GO TO 77
6      IF[MOD[K,2]]32,33,32
32     TAU=N+CC/[A[1]-AA[1]]
       CORRECT=FLOAT[N]-TAU
       GO TO 35
33     TAU=N+CC/[B[1]-BB[1]]
       CORRECT=FLOAT[N]-TAU
35     DO 800 I=1,MAXV
       A[I]=AA[I]+CORRECT*[A[I]-AA[I]]
800    B[I]=BB[I]+CORRECT*[B[I]-BB[I]]
       IF [SENSE LIGHT 1] 20,21
20     XX=TAU
21     YY=TAU/XX
50     PRINT 16,K,TAU,YY
16     FORMAT[/$K=$,I3,5X,$TAU=$,F10.6,5X,$REL.TRANS.TIME=$,F10.6/]
       PRINT 60
60     FORMAT[$END$]
       STOP
       END
‡
```

Variables are:

CC	concentration of the reactive species at the surface of the electrode (zero-th compartment)
NMAX	total (cumulative) number of time units in KK cycles
MAXV	maximum number of compartments affected by concentration changes defined[14] as MAXV = 6 * SQRT (D * NMAX), where D is the larger of two diffusion coefficients

Print-out values:

KK	number of cycles
N	number of time units describing a transition time
YY	relative transition time.

The computer program is designed to calculate changes in concentration of the reactant and the product of the electrochemical reaction due to current flow, diffusion (DO 8 loop) and the second order chemical reaction (DO 13 loop). TAU is the corrected transition time if CC, after a certain number of time units, becomes negative. The DO 800 loop makes the necessary corrections in all the compartments.

Calculations have been done using a CAE-90-40 computer. One set of 20 points, as that shown in Table IV required approximately 60 minutes computing time.

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IZVOD

Ciklička kronopotenciometrija. Određivanje vrste i brzine kemijskih transformacija drugog reda koje slijede prijenos elektrona

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Ciklička kronopotenciometrija je do sada uspješno primijenjivana tehnika u proučavanju kinetike kemijskih reakcija prvog reda koje slijede prijenos elektrona. Opisan je matematički postupak, baziran na Feldbergovoj metodi digitalne simulacije. S pomoću njega možemo iz podataka dobivenih u jednom pokusu odrediti tip i koeficijent brzine kemijske reakcije drugoga reda. Prikazani su diagnostički kriteriji za kinetičku reakciju kao i za reakciju disproporcionacije, ako one uslijede iza prijenosa elektrona. U tu svrhu napisan je kompjutorski program u Fortran II jeziku. Metoda računanja i tehnika mjerenja ispitani su na primjeru redukcije uraniuma(VI) i naknadne disproporcionacije uraniuma(V). Koeficijent brzine takve kemijske reakcije u području oko 10 l mol^{-1} sek^{-1} može se odrediti s pogreškom od ± 2⁰/₀. Procjenom točnosti numeričke metode s jedne strane, a tehnike cikličke kronopotenciometrije s druge, može se mjeriti koeficijente brzine reakcije u području od 10^{-1} do 10^5 l mol^{-1} sek^{-1}.

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