

## POLARIZATION OF AN ELECTRODE WITH A POTENTIOSTATIC PULSE IN THE FORM OF AN EQUILATERAL TRIANGLE

V. MAREČEK and J. HONZ

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, Prague 10*

Received May 3rd, 1972

The present work brings characteristic parameters of current-voltage curves obtained by numerical solution of an integral equation describing the behaviour of an electrode during polarization with a potentiostatic pulse in the form of an equilateral triangle. A simple electrochemical reaction was assumed. Tabulated data found by a computer can be used in determining electrochemical rate constants from experimental data.

The behaviour of an electrode polarized with a potentiostatic pulse in the form of an equilateral triangle was studied under the following assumptions: A single electrode reaction proceeds at the electrode in the envisaged potential range,



and the current density on the electrode is at any instant given by the equation

$$i = -nFk_s [c_{\text{ox}}^0 \exp(-anF(E - E^0)/RT) - c_{\text{red}}^0 \exp((1 - \alpha)nF(E - E^0)/RT)], \quad (1)$$

where  $k_s$  denotes rate constant of the electrode reaction at standard potential and the superscript 0 concentration at the electrode surface. The dependence of potential  $E$  on time  $t$  is given by

$$E(t) = E_1 - vt \quad \text{for } t \in \langle 0; (E_1 - E_2)/v \rangle, \quad (2)$$

$$E(t) = 2E_2 - E_1 + vt \quad \text{for } t > (E_1 - E_2)/v, \quad (3)$$

where  $v > 0$  and  $E_1$  denotes equilibrium electrode potential corresponding to concentrations  $c_{\text{ox}}$  and  $c_{\text{red}}$  of the oxidized and reduced forms:

$$E_1 = (RT/nF) \ln (c_{\text{ox}}/c_{\text{red}}) + E^0. \quad (4)$$

The electrode is plane and both forms, Ox and Red, of the depolarizer are transported

to the interface by diffusion alone (the effect of electric field can be neglected). At time  $t = 0$ , no current flows and  $c_{\text{ox}}^0 = c_{\text{ox}}$  (bulk concentration),  $c_{\text{red}}^0 = c_{\text{red}}$ .

*Time dependence of current density.* With the mentioned assumptions, the following equation applies:

$$i = -nF c_{\text{ox}} (nFD_{\text{ox}}v/RT)^{1/2} \Psi[nF(E_p + vt - E_1)/RT], \quad (5)$$

where  $E_p$  denotes polarographic half-wave potential defined as

$$E_p = E^0 + (RT/nF) \ln \sqrt{(D_{\text{red}}/D_{\text{ox}})}. \quad (6)$$

$D_{\text{ox}}$  and  $D_{\text{red}}$  denote diffusion coefficients of Ox and Red and the function  $\Psi$  is the solution of the integral equation

$$\bar{L}(\Psi)(X) = \Psi(X)/A + \int_{-\infty}^{+\infty} K(X, \xi) \Psi(\xi) d\xi = Q(X); \quad (7)$$

the functions  $K$  and  $Q$  are defined as follows:

$$K(X, \xi) = P(X)/[\sqrt{\pi} \sqrt{(X - \xi)}] \text{ for } X_1 < \xi < X, \text{ otherwise } K(X, \xi) = 0,$$

$$P(X) = \exp(\alpha X) + \exp[-(1 - \alpha)X] \text{ for } X \leq X_2,$$

$$P(X) = \exp[\alpha(2X_2 - X)] + \exp[-(1 - \alpha)(2X_2 - X)] \text{ for } X_2 < X,$$

$$Q(X) = 0 \text{ for } X \leq X_1,$$

$$Q(X) = \exp(\alpha X) - \exp(X_1) \exp[-(1 - \alpha)X] \text{ for } X_1 < X \leq X_2,$$

$$Q(X) = \exp[\alpha(2X_2 - X)] - \exp(X_1) \exp[-(1 - \alpha)(2X_2 - X)] \text{ for } X_2 < X.$$

The linear operator  $\bar{L}$ , function  $Q$  and hence also the sought function  $\Psi$  depend on the following parameters:

$$A = k_s / (nFD_{\text{red}}^\alpha D_{\text{ox}}^{1-\alpha} v / RT)^{1/2}, \quad (8)$$

$$X_1 = nF(E_p - E_1)/RT, \quad X_2 = nF(E_p - E_2)/RT \quad (9), (10)$$

and  $\alpha$ . Our solution was obtained from Eqs (1)–(3) and the Fick diffusion equations for Ox and Red by the method used already by Matsuda and Ayabe<sup>1</sup> in calculating current–time curves for an electrode polarized with a linear potentiostatic pulse. For a sufficiently large negative  $X_1$  and positive  $X_2$ , the function  $\Psi$  has a maximum  $\Psi_K$  in the point  $X_K < X_2$  corresponding to a cathodic minimum of current density (cathodic peak), and a minimum  $\Psi_A$  at  $X_A > X_2$  corresponding to an anodic current density maximum. Let  $X_{\text{KP}} < X_K$  be a point such that  $\Psi(X_{\text{KP}}) = \frac{1}{2}\Psi_K$ .

The quantities

$$D_{\text{AK}} = X_K + X_A - 2X_2, \quad D_{\text{KKP}} = X_K - X_{\text{KP}}, \quad (11), (12)$$

$$D_{\text{KR}} = X_K(A) - \lim_{\Lambda \rightarrow \infty} X_K(\Lambda) \quad (13)$$

are experimentally accessible since (according to Eqs (2)–(4)) the first one is equal

to  $nF/RT$  times the difference between the potentials of the anodic and cathodic peaks, the second is  $nF/RT$  times the difference between the potential in one half of the cathodic peak (before the peak is reached) and the peak potential, and the third is  $nF/RT$  times the difference between the cathodic peak potentials in the reversible case (small rate of potential change,  $v$ ) and in the actual case (at the given rate  $v$ ). Also the quantities

$$Q_{AK} = -\Psi_A/\Psi_K, \quad Q_{KR} = \Psi_K/\lim_{\Lambda \rightarrow \infty} \Psi_K(\Lambda) \quad (14), (15)$$

are experimentally accessible since the first one is equal to the ratio of absolute values of the anodic and cathodic peak current densities and the second is  $(v_R/v)^{1/2}$  times the ratio of current densities at the given rate of potential change,  $v$ , and at a small rate,  $v_R$ , corresponding to the reversible case. Each of the quantities (11)–(15) is a function of  $\alpha$ ,  $\Lambda$ ,  $X_1$  and  $X_2$ . With a sufficiently large negative  $X_1$ , their values are practically independent of  $X_1$ . We assumed  $X_1 = -15$  in the numerical calculations; the influence of this parameter on the mentioned quantities will be discussed in a later communication. It follows from Eq. (7) as well as from the physical substance of the problem that the functions  $\Psi$  corresponding to the same values of  $\alpha$ ,  $\Lambda$ ,  $X_1$  but different values of  $X_2$  are equal in all points  $X$  lying to the left from the smaller of both  $X_2$  values; hence their maxima have the same coordinate  $X_K$ . This makes it possible to find the function corresponding to the given  $\alpha$ ,  $\Lambda$ ,  $X_1$  and  $X_2 = X_K + D_{2,K}$ , where  $D_{2,K}$  is an arbitrary constant, from the known value of  $X_K$  for  $X_2 \rightarrow \infty$ .  $D_{2,K}$  is equal to  $nF/RT$  times the difference between the cathodic peak potential and  $E_2$  defined by Eqs (2) and (3). We set  $D_{2,K} = 4$ ; the dependence of  $\Psi$  on  $D_{2,K}$  will be discussed in a later communication.

*Numerical solution.* From the definition of the function  $\Psi$ , Eq. (7), it follows that  $\Psi(X) = 0$  for any  $X \leq X_1$ . The function  $\Psi$  was approximated by the sum  $\sum_{N=1}^{\infty} \Psi_N$ , where  $\Psi_N$  means a second-degree polynomial in the interval  $I_N \equiv (X_1 + (2N-2)H; X_1 + 2NH)$ ,  $H$  denotes a small positive number; for  $X$  outside this interval is  $\Psi_N = 0$ . A condition was postulated that the  $\bar{L}$  transform of the approximation attains in the mid- and end points of each interval  $I_N$  the same value as the function  $Q$  and that the approximation is continuous in the point  $X_1$  and in the end points of the intervals  $I_N$ . If we write

$$\Psi_N = \sum_{M=1}^3 B_{N,M} \omega_{N,M}, \quad (16)$$

where  $\omega_{N,M}(X) = (X - X_1 - (2N-2)H)^{M-1}$  for  $X \in I_N$  and  $\omega_{N,M}(X) = 0$  for the other case, then the mentioned postulates lead to three linear equations for each of the vectors  $B_N = (B_{N,M})$ ,  $M = 1, 2, 3$ :

$$\sum_{M=1}^3 \beta_{N,L,M} B_{N,M} = C_{N,L}, \quad L = 1, 2, 3 \quad (17)$$

with the following definitions:

$$\beta_{N,L,M} = \bar{L}(\omega_{N,M}) (X_1 + (2N - 2 + L)H) = (LH)^{M-1}/A + Q(X_1 + (2N - 2 + L)H) 2^M \cdot$$

$$\cdot [(LH)^{M-1/2}/M \sqrt{\pi}] \prod_{S=1}^M (M - S + 1)/(2S - 1) \text{ for } L = 1 \text{ and } 2, \beta_{N,3,M} = \lim_{\varepsilon \rightarrow 0^+} \omega_{N,M}(X_1 +$$

$$+ (2N - 2)H + \varepsilon) = 1 \text{ for } M = 1, \text{ and } 0 \text{ for } M = 2, 3, C_{N,L} = Q - \bar{L} \left( \sum_{J=1}^{N-1} \Psi_J \right) (X_1 +$$

$$+ (2N - 2 + L)H) = Q(X_1 + (2N - 2 + L)H) + [P(X_1 + (2N - 2 + L)H)/\sqrt{\pi}] \cdot$$

$$\cdot \sum_{J=1}^{N-1} \sum_{M=1}^3 B_{J,M}(2^M/M) (\sqrt{H})^{M-1} \left[ \sum_{R=1}^M (2N - 2J + L - 2)^{R-1/2} \cdot \prod_{S=1}^R (M - S + 1)/(2S - 1) \right.$$

$$\left. - (2N - 2J + L)^{M-1/2} \prod_{S=1}^M (M - S + 1)/(2S - 1) \right], L = 1, 2, N \geq 2, C_{1,L} = Q(X_1 + LH)$$

$$\text{for } L = 1 \text{ and } 2, C_{N,3} = \Psi_{N-1}(X_1 + (2N - 2)H) = \sum_{M=1}^3 B_{N-1,M}(2H)^{M-1} \text{ for } N \geq 2,$$

and  $C_{1,3} = 0$ . The right sides of Eqs (17) for the vector  $B_N$  are functions of vectors  $B_J$  ( $J \leq N - 1$ ). The approximation of the function  $\Psi$  is found by solving Eqs (17) in turn for  $N = 1, 2, 3$  and so on. The value of  $B_{N,1}$  is equal to the approximation in the end point of the interval  $I_{N-1}$ . The coordinate and value of the maximum are determined as follows. First, the smallest natural  $N$  is found for which  $B_{N,1} < B_{N-1,1}$ . The coordinate of the maximum is then in the interval  $I_{N-2} \cup I_{N-1}$  and restriction of the approximation to this interval means restriction of the function  $\Psi_{N-2} + \Psi_{N-1}$  to this interval, where the coordinate of the maximum can then be found according to the common rules of mathematical analysis. The coordinate and value of the minimum are found analogously. We chose  $H = 0.25$  (the coordinates of the maximum and minimum calculated for  $H = 0.5$  and for  $H = 0.25$  do not differ by more than 0.025).

## RESULTS

Characteristic parameters of current-voltage curves are tabulated at the end of this paper. It should be added that with decreasing  $A$ ,  $Q_{KR}$  approaches  $1.1109 \sqrt{\alpha}$ ,  $\Psi_K$   $0.4958 \sqrt{\alpha}$ ,  $D_{KKR}$   $1.85/\alpha$  and the dependence of  $D_{KR}$  on  $\log A$  approaches asymptotically the straight line  $D_{KR} = -(\ln 10)(\log A)/\alpha + (\ln 10)(\log \alpha)/2\alpha + 0.78/\alpha - 1.1127$ . This follows from the previous results<sup>1,2</sup> concerning the so-called irreversible reaction course during polarization of an electrode with a linear potentiostatic pulse.

The electrochemical rate constant can be calculated as follows. Two of the quantities  $D_{AK}$ ,  $D_{KKP}$ ,  $D_{KR}$ ,  $Q_{AK}$  and  $Q_{KR}$  are selected and evaluated from the experimental current-voltage curve. The sets of all possible pairs of  $\alpha$  and  $A$  values corresponding to the values of the selected quantities are found; the pair  $\alpha$ ,  $A$  that belongs to both of these sets corresponds to the given rate of change of potential. The remaining of  $D_{AK}$ ,  $D_{KKP}$ ,  $D_{KR}$ ,  $Q_{AK}$  and  $Q_{KR}$  can be used to check the correctness of the found  $\alpha$  and  $A$  values. The values of  $\Psi_K$  or  $\Psi_A$  are then found from the tables,  $D_{ox}$  and  $k_s$  are calculated from Eqs (5) and (8).

TABLES  
Characteristic Parameters of Current-Voltage Curves

$\alpha$	$\psi_K$	$\psi_A$	$Q_{KR}$	$Q_{AK}$	$X_K$	$D_{AK}$	$D_{KKP}$	$D_{KR}$
$\log A = \infty$								
0.1-0.9	0.4463	-0.2775	1	0.6218	1.1127	2.30	2.21	0
$\log A = 1.0$								
0.9	0.4480	-0.2668	1.0038	0.5955	1.18	2.44	2.19	0.07
0.8	0.4465	-0.2691	1.0004	0.6027	1.19	2.44	2.21	0.08
0.7	0.4449	-0.2710	0.9969	0.6091	1.20	2.48	2.23	0.09
0.6	0.4431	-0.2727	0.9928	0.6154	1.21	2.49	2.24	0.10
0.5	0.4410	-0.2740	0.9881	0.6213	1.21	2.49	2.26	0.10
0.4	0.4387	-0.2750	0.9830	0.6269	1.21	2.48	2.27	0.10
0.3	0.4360	-0.2757	0.9769	0.6323	1.21	2.48	2.28	0.10
0.2	0.4329	-0.2759	0.9700	0.6373	1.20	2.46	2.29	0.09
0.1	0.4294	-0.2758	0.9621	0.6423	1.18	2.44	2.29	0.07
$\log A = 0.9$								
0.9	0.4484	-0.2641	1.0047	0.5890	1.20	2.48	2.19	0.03
0.8	0.4466	-0.2670	1.0007	0.5979	1.21	2.50	2.21	0.10
0.7	0.4446	-0.2695	0.9962	0.6062	1.22	2.52	2.23	0.11
0.6	0.4423	-0.2715	0.9910	0.6138	1.23	2.53	2.25	0.12
0.5	0.4397	-0.2732	0.9852	0.6213	1.24	2.53	2.27	0.12
0.4	0.4368	-0.2744	0.9787	0.6282	1.24	2.53	2.29	0.13
0.3	0.4334	-0.2753	0.9711	0.6352	1.23	2.52	2.30	0.12
0.2	0.4296	-0.2756	0.9626	0.6415	1.22	2.50	2.31	0.11
0.1	0.4252	-0.2753	0.9527	0.6475	1.20	2.48	2.31	0.09
$\log A = 0.8$								
0.9	0.4489	-0.2609	1.0058	0.5812	1.22	2.52	2.19	0.11
0.8	0.4467	-0.2644	1.0009	0.5919	1.24	2.55	2.21	0.12
0.7	0.4442	-0.2675	0.9953	0.6022	1.25	2.57	2.24	0.14
0.6	0.4414	-0.2700	0.9890	0.6117	1.26	2.58	2.26	0.15
0.5	0.4381	-0.2721	0.9816	0.6211	1.27	2.58	2.29	0.15
0.4	0.4345	-0.2737	0.9736	0.6299	1.27	2.58	2.31	0.16
0.3	0.4302	-0.2747	0.9639	0.6385	1.26	2.57	2.32	0.15
0.2	0.4255	-0.2751	0.9534	0.6465	1.25	2.55	2.33	0.14
0.1	0.4201	-0.2747	0.9413	0.6539	1.22	2.52	2.33	0.11
$\log A = 0.7$								
0.9	0.4495	-0.2569	1.0072	0.5715	1.25	2.56	2.18	0.14
0.8	0.4468	-0.2613	1.0011	0.5848	1.27	2.60	2.21	0.15
0.7	0.4437	-0.2650	0.9942	0.5973	1.28	2.62	2.24	0.17

## TABLES

(Continued)

$\alpha$	$\psi_K$	$\psi_A$	$Q_{KR}$	$Q_{AK}$	$X_K$	$D_{AK}$	$D_{KKP}$	$D_{KR}$
$\log A = 0.7$								
0.6	0.4402	-0.2681	0.9863	0.6090	1.30	2.64	2.28	0.18
0.5	0.4362	-0.2707	0.9774	0.6206	1.30	2.64	2.31	0.19
0.4	0.4316	-0.2726	0.9671	0.6316	1.31	2.64	2.33	0.19
0.3	0.4264	-0.2739	0.9554	0.6424	1.30	2.63	2.35	0.19
0.2	0.4205	-0.2744	0.9422	0.6526	1.28	2.60	2.36	0.17
0.1	0.4138	-0.2740	0.9272	0.6622	1.25	2.57	2.36	0.13
$\log A = 0.6$								
0.9	0.4503	-0.2521	1.0090	0.5598	1.28	2.62	2.17	0.17
0.8	0.4469	-0.2573	1.0013	0.5757	1.30	2.66	2.21	0.19
0.7	0.4430	-0.2619	0.9926	0.5912	1.32	2.69	2.25	0.21
0.6	0.4387	-0.2657	0.9830	0.6057	1.34	2.72	2.29	0.23
0.5	0.4338	-0.2689	0.9720	0.6199	1.35	2.73	2.33	0.24
0.4	0.4281	-0.2713	0.9592	0.6337	1.35	2.73	2.36	0.24
0.3	0.4216	-0.2728	0.9447	0.6471	1.35	2.70	2.39	0.23
0.2	0.4143	-0.2735	0.9283	0.6602	1.32	2.66	2.40	0.21
0.1	0.4062	-0.2730	0.9102	0.6721	1.28	2.62	2.40	0.17
$\log A = 0.5$								
0.9	0.4511	-0.2461	1.0108	0.5456	1.32	2.68	2.16	0.21
0.8	0.4469	-0.2525	1.0013	0.5650	1.35	2.75	2.21	0.23
0.7	0.4423	-0.2581	0.9910	0.5835	1.37	2.80	2.26	0.26
0.6	0.4369	-0.2629	0.9789	0.6017	1.39	2.83	2.31	0.28
0.5	0.4308	-0.2668	0.9653	0.6193	1.41	2.84	2.35	0.29
0.4	0.4239	-0.2698	0.9498	0.6365	1.41	2.84	2.40	0.30
0.3	0.4159	-0.2717	0.9319	0.6533	1.40	2.82	2.43	0.29
0.2	0.4069	-0.2723	0.9117	0.6692	1.37	2.77	2.45	0.26
0.1	0.3971	-0.2715	0.8898	0.6837	1.32	2.69	2.44	0.21
$\log A = 0.4$								
0.9	0.4521	-0.2391	1.0130	0.5289	1.36	2.79	2.15	0.25
0.8	0.4470	-0.2468	1.0016	0.5521	1.40	2.87	2.21	0.28
0.7	0.4413	-0.2536	0.9888	0.5747	1.43	2.92	2.27	0.31
0.6	0.4348	-0.2595	0.9742	0.5968	1.45	2.95	2.33	0.34
0.5	0.4273	-0.2643	0.9574	0.6185	1.47	2.96	2.38	0.36
0.4	0.4188	-0.2679	0.9384	0.6397	1.48	2.95	2.44	0.37
0.3	0.4090	-0.2702	0.9164	0.6606	1.47	2.93	2.48	0.36
0.2	0.3981	-0.2710	0.8920	0.6807	1.44	2.88	2.50	0.32
0.1	0.3861	-0.2698	0.8651	0.6988	1.37	2.80	2.50	0.25

TABLES  
 (Continued)

$\alpha$	$\psi_K$	$\psi_A$	$Q_{KR}$	$Q_{AK}$	$X_K$	$D_{AK}$	$D_{KKP}$	$D_{KR}$
$\log A = 0.3$								
0.9	0.4532	-0.2308	1.0155	0.5093	1.42	2.90	2.14	0.31
0.8	0.4470	-0.2400	1.0016	0.5369	1.46	2.98	2.20	0.35
0.7	0.4401	-0.2481	0.9861	0.5637	1.50	3.05	2.28	0.38
0.6	0.4322	-0.2554	0.9684	0.5909	1.54	3.11	2.36	0.43
0.5	0.4232	-0.2613	0.9482	0.6174	1.58	3.14	2.44	0.46
0.4	0.4128	-0.2658	0.9249	0.6439	1.59	3.14	2.51	0.48
0.3	0.4009	-0.2686	0.8983	0.6700	1.58	3.11	2.57	0.47
0.2	0.3876	-0.2692	0.8685	0.6945	1.52	3.02	2.59	0.41
0.1	0.3733	-0.2675	0.8364	0.7166	1.42	2.91	2.57	0.31
$\log A = 0.2$								
0.9	0.4544	-0.2212	1.0181	0.4868	1.48	3.01	2.12	0.37
0.8	0.4470	-0.2320	1.0016	0.5190	1.54	3.16	2.21	0.43
0.7	0.4387	-0.2420	0.9830	0.5516	1.60	3.25	2.31	0.49
0.6	0.4293	-0.2507	0.9619	0.5840	1.65	3.30	2.41	0.54
0.5	0.4184	-0.2578	0.9375	0.6162	1.70	3.33	2.50	0.58
0.4	0.4059	-0.2632	0.9095	0.6484	1.72	3.34	2.60	0.61
0.3	0.3915	-0.2666	0.8772	0.6810	1.71	3.30	2.67	0.60
0.2	0.3754	-0.2674	0.8411	0.7123	1.65	3.22	2.70	0.53
0.1	0.3583	-0.2645	0.8028	0.7382	1.49	3.03	2.65	0.38
$\log A = 0.1$								
0.9	0.4557	-0.2104	1.0211	0.4617	1.58	3.20	2.13	0.47
0.8	0.4470	-0.2230	1.0016	0.4989	1.65	3.34	2.23	0.54
0.7	0.4372	-0.2347	0.9796	0.5368	1.72	3.48	2.33	0.60
0.6	0.4260	-0.2450	0.9545	0.5751	1.78	3.55	2.45	0.67
0.5	0.4130	-0.2536	0.9254	0.6140	1.83	3.58	2.57	0.72
0.4	0.3980	-0.2601	0.8918	0.6535	1.86	3.58	2.69	0.75
0.3	0.3808	-0.2642	0.8532	0.6938	1.86	3.55	2.78	0.75
0.2	0.3616	-0.2649	0.8102	0.7326	1.79	3.45	2.83	0.68
0.1	0.3413	-0.2613	0.7647	0.7656	1.61	3.24	2.78	0.50
$\log A = 0.0$								
0.9	0.4572	-0.1981	1.0244	0.4333	1.69	3.38	2.12	0.57
0.8	0.4471	-0.2126	1.0018	0.4755	1.76	3.60	2.23	0.65
0.7	0.4355	-0.2262	0.9758	0.5194	1.84	3.73	2.35	0.73
0.6	0.4223	-0.2384	0.9462	0.5645	1.92	3.82	2.49	0.80
0.5	0.4069	-0.2486	0.9117	0.6110	1.99	3.87	2.64	0.87

TABLES  
 (Continued)

$\alpha$	$\psi_K$	$\psi_A$	$Q_{KR}$	$Q_{AK}$	$X_K$	$D_{AK}$	$D_{KKP}$	$D_{KR}$
$\log A = 0.0$								
0.4	0.3892	-0.2565	0.8721	0.6590	2.05	3.88	2.80	0.94
0.3	0.3688	-0.2613	0.8264	0.7085	2.06	3.85	2.93	0.95
0.2	0.3460	-0.2617	0.7753	0.7564	1.96	3.72	2.99	0.85
0.1	0.3223	-0.2569	0.7222	0.7971	1.74	3.47	2.94	0.63
$\log A = -0.1$								
0.9	0.4588	-0.1847	1.0280	0.4026	1.80	3.61	2.11	0.69
0.8	0.4470	-0.2009	1.0016	0.4494	1.89	3.88	2.23	0.78
0.7	0.4335	-0.2166	0.9713	0.4997	1.98	4.04	2.37	0.87
0.6	0.4182	-0.2310	0.9370	0.5524	2.09	4.17	2.55	0.98
0.5	0.4004	-0.2432	0.8972	0.6074	2.20	4.23	2.74	1.09
0.4	0.3798	-0.2525	0.8510	0.6648	2.29	4.27	2.95	1.18
0.3	0.3559	-0.2583	0.7974	0.7258	2.32	4.25	3.14	1.21
0.2	0.3291	-0.2588	0.7374	0.7864	2.23	4.10	3.23	1.11
0.1	0.3015	-0.2514	0.6756	0.8338	1.90	3.73	3.11	0.79
$\log A = -0.2$								
0.9	0.4603	-0.1701	1.0314	0.3695	1.92	3.87	2.10	0.81
0.8	0.4467	-0.1883	1.0009	0.4215	2.03	4.21	2.24	0.92
0.7	0.4314	-0.2064	0.9666	0.4784	2.17	4.44	2.42	1.05
0.6	0.4140	-0.2230	0.9276	0.5386	2.30	4.57	2.61	1.19
0.5	0.3937	-0.2369	0.8821	0.6017	2.43	4.65	2.84	1.32
0.4	0.3700	-0.2481	0.8290	0.6705	2.57	4.72	3.11	1.45
0.3	0.3425	-0.2552	0.7674	0.7451	2.66	4.72	3.39	1.54
0.2	0.3112	-0.2553	0.6973	0.8204	2.56	4.56	3.53	1.45
0.1	0.2793	-0.2453	0.6258	0.8783	2.12	4.08	3.36	1.01
$\log A = -0.3$								
0.9	0.4616	-0.1550	1.0343	0.3358	2.07	4.18	2.09	0.96
0.8	0.4465	-0.1751	1.0004	0.3922	2.21	4.62	2.26	1.10
0.7	0.4294	-0.1954	0.9621	0.4551	2.36	4.89	2.44	1.25
0.6	0.4096	-0.2141	0.9178	0.5227	2.52	5.03	2.67	1.40
0.5	0.3869	-0.2305	0.8669	0.5958	2.72	5.15	2.97	1.60
0.4	0.3603	-0.2433	0.8073	0.6753	2.91	5.25	3.31	1.80
0.3	0.3291	-0.2519	0.7374	0.7654	3.08	5.32	3.70	1.97
0.2	0.2933	-0.2526	0.6572	0.8612	3.04	5.20	3.96	1.93
0.1	0.2564	-0.2385	0.5745	0.9302	2.43	4.51	3.69	1.31



## TABLES

(Continued)

$\alpha$	$\psi_K$	$\psi_A$	$Q_{KR}$	$Q_{AK}$	$X_K$	$D_{AK}$	$D_{KKP}$	$D_{KR}$
$\log A = -0.4$								
0.9	0.4630	-0.1397	1.0374	0.3017	2.25	4.53	2.09	1.13
0.8	0.4463	-0.1613	1.0000	0.3614	2.39	5.08	2.26	1.28
0.7	0.4272	-0.1841	0.9572	0.4309	2.57	5.41	2.47	1.46
0.6	0.4055	-0.2053	0.9086	0.5877	2.79	5.59	2.74	1.67
0.5	0.3803	-0.2235	0.8521	0.8521	3.02	5.72	3.08	1.91
0.4	0.3511	-0.2385	0.7867	0.6793	3.32	5.88	3.53	2.20
0.3	0.3166	-0.2490	0.7094	0.7865	3.62	6.06	4.08	2.51
0.2	0.2763	-0.2515	0.6191	0.9102	3.78	6.10	4.60	2.66
0.1	0.2333	-0.2322	0.5227	0.9953	2.91	5.15	4.19	1.80
$\log A = -0.5$								
0.9	0.4643	-0.1243	1.0403	0.2677	2.41	4.93	2.08	1.30
0.8	0.4459	-0.1477	0.9991	0.3312	2.60	5.71	2.27	1.49
0.7	0.4252	-0.1729	0.9527	0.4066	2.81	6.08	2.51	1.70
0.6	0.4015	-0.1961	0.8996	0.4884	3.06	6.22	2.80	1.95
0.5	0.3743	-0.2165	0.8387	0.5784	3.38	6.37	3.20	2.27
0.4	0.3428	-0.2334	0.7681	0.6809	3.78	6.59	3.76	2.67
0.3	0.3057	-0.2462	0.6850	0.8054	4.28	6.93	4.53	3.17
0.2	0.2616	-0.2522	0.5862	0.9641	4.82	7.33	5.51	3.71
0.1	0.2114	-0.2296	0.4737	1.0861	3.82	6.22	5.11	2.71
$\log A = -0.6$								
0.9	0.4652	-0.1095	1.0423	0.2354	2.61	5.39	2.08	1.50
0.8	0.4456	-0.1346	0.9984	0.3021	2.82	6.49	2.28	1.71
0.7	0.4233	-0.1620	0.9485	0.3827	3.06	6.84	2.53	1.95
0.6	0.3980	-0.1874	0.8918	0.4709	3.37	6.94	2.86	2.26
0.5	0.3690	-0.2095	0.8268	0.5678	3.77	7.08	3.32	2.65
0.4	0.3357	-0.2282	0.7522	0.6798	4.29	7.37	3.98	3.18
0.3	0.2968	-0.2433	0.6650	0.8197	5.02	7.90	4.97	3.91
0.2	0.2504	-0.2540	0.5611	1.0144	6.12	8.82	6.58	5.01
0.1	0.1931	-0.2443	0.4327	1.2651	6.54	9.12	7.79	5.42
$\log A = -0.7$								
0.9	0.4663	-0.0955	1.0448	0.2048	2.81	6.00	2.08	1.70
0.8	0.4452	-0.1226	0.9975	0.2754	3.04	7.52	2.28	1.93
0.7	0.4216	-0.1522	0.9447	0.3610	3.34	7.74	2.56	2.23
0.6	0.3949	-0.1791	0.8848	0.4535	3.70	7.74	2.92	2.59
0.5	0.3646	-0.2026	0.8169	0.5557	4.18	7.84	3.42	3.06

TABLES  
 (Continued)

$\alpha$	$\psi_K$	$\psi_A$	$Q_{KR}$	$Q_{AK}$	$X_K$	$D_{AK}$	$D_{KKP}$	$D_{KR}$
$\log A = -0.7$								
0.4	0.3300	-0.2229	0.7394	0.6755	4.83	8.21	4.17	3.72
0.3	0.2899	-0.2401	0.6496	0.8282	5.81	8.95	5.39	4.70
0.2	0.2424	-0.2544	0.5431	1.0495	7.47	10.40	7.57	6.36
0.1	0.1821	-0.2619	0.4080	1.4382	10.43	13.19	11.52	9.32
$\log A = -0.8$								
0.9	0.4670	-0.0826	1.0464	0.1769	3.01	6.78	2.06	1.90
0.8	0.4450	-0.1125	0.9971	0.2528	3.29	8.92	2.30	2.18
0.7	0.4201	-0.1436	0.9413	0.3418	3.62	8.77	2.58	2.51
0.6	0.3923	-0.1714	0.8790	0.4369	4.04	8.59	2.95	2.92
0.5	0.3610	-0.1961	0.8089	0.5432	4.60	8.69	3.50	3.49
0.4	0.3255	-0.2176	0.7293	0.6685	5.39	9.10	4.32	4.28
0.3	0.2847	-0.2364	0.6379	0.8303	6.62	10.03	5.70	5.50
0.2	0.2367	-0.2531	0.5304	1.0693	8.78	11.96	8.35	7.67
0.1	0.1753	-0.2674	0.3928	1.5254	13.49	16.45	14.26	12.37
$\log A = -0.9$								
0.9	0.4677	-0.0713	1.0479	0.1524	3.25	8.04	2.08	2.14
0.8	0.4446	-0.1043	0.9962	0.2346	3.54	10.46	2.29	2.42
0.7	0.4190	-0.1363	0.9388	0.3253	3.91	9.90	2.59	2.80
0.6	0.3903	-0.1648	0.8745	0.4222	4.39	9.54	2.99	3.28
0.5	0.3582	-0.1900	0.8026	0.5304	5.04	9.54	3.56	3.92
0.4	0.3221	-0.2123	0.7217	0.6591	5.96	10.01	4.44	4.85
0.3	0.2810	-0.2321	0.6296	0.8260	7.42	11.11	5.92	6.30
0.2	0.2327	-0.2502	0.5214	1.0752	10.03	13.45	8.87	8.92
0.1	0.1705	-0.2677	0.3820	1.5701	16.20	19.39	16.43	15.09
$\log A = -1.0$								
0.9	0.4683	-0.0623	1.0493	0.1330	3.46	12.13	2.06	2.35
0.8	0.4445	-0.0983	0.9960	0.2211	3.81	12.24	2.31	2.69
0.7	0.4180	-0.1303	0.9366	0.3117	4.22	11.05	2.61	3.11
0.6	0.3886	-0.1589	0.8707	0.4089	4.76	10.47	3.03	3.65
0.5	0.3560	-0.1844	0.7977	0.5180	5.48	10.45	3.61	4.37
0.4	0.3196	-0.2072	0.7161	0.6483	6.54	10.95	4.52	5.43
0.3	0.2783	-0.2279	0.6236	0.8189	8.21	12.22	6.06	7.10
0.2	0.2298	-0.2462	0.5149	1.0714	11.26	14.95	9.15	10.14
0.1	0.1671	-0.2660	0.3744	1.5919	18.76	22.18	17.99	17.65

TABLES  
 (Continued)

$\alpha$	$\psi_K$	$\psi_A$	$Q_{KR}$	$Q_{AK}$	$X_K$	$D_{AK}$	$D_{KKP}$	$D_{KR}$
$\log A = -1.1$								
0.9	0.4687	-0.0571	1.0502	0.1218	3.71	17.29	2.07	2.60
0.8	0.4441	-0.0934	0.9951	0.2103	4.07	14.13	2.30	2.95
0.7	0.4172	-0.1253	0.9348	0.3003	4.52	12.16	2.61	3.41
0.6	0.3874	-0.1538	0.8680	0.3970	5.13	11.44	3.05	4.02
0.5	0.3544	-0.1793	0.7941	0.5059	5.94	11.36	3.64	4.83
0.4	0.3178	-0.2022	0.7121	0.6363	7.13	11.91	4.57	6.01
0.3	0.2763	-0.2229	0.6191	0.8067	8.99	13.31	6.12	7.88
0.2	0.2276	-0.2422	0.5100	1.0641	12.45	16.38	9.25	11.34
0.1	0.1646	-0.2624	0.3688	1.5942	21.23	24.85	18.68	20.12
$\log A = -1.2$								
0.9	0.4691	-0.0533	1.0511	0.1136	3.94	21.06	2.06	2.83
0.8	0.4441	-0.0896	0.9951	0.2018	4.34	15.48	2.31	3.23
0.7	0.4166	-0.1212	0.9335	0.2909	4.85	13.40	2.63	3.73
0.6	0.3864	-0.1490	0.8658	0.3856	5.49	12.51	3.05	4.38
0.5	0.3533	-0.1746	0.7916	0.4942	6.40	12.27	3.67	5.29
0.4	0.3165	-0.1975	0.7092	0.6240	7.71	12.90	4.60	6.59
0.3	0.2750	-0.2182	0.6162	0.7935	9.78	14.40	6.16	8.67
0.2	0.2261	-0.2373	0.5066	1.0495	13.63	17.82	9.28	12.52
0.1	0.1627	-0.2579	0.3646	1.5851	23.66	27.53	18.22	22.54

The tables given above were used already in our earlier work<sup>3</sup> in determining the rate constant of the reaction  $\text{Li}^+ + x \text{Hg} + e = \text{LiHg}_x$  in propylene carbonate by the linear pulse method. Determination of the mentioned rate constant by the triangular potentiostatic pulse method, design of a suitable analogue circuit and further use of the tables will be the subject of a subsequent communication.

## REFERENCES

1. Matsuda H., Ayabe Y.: *Z. Elektrochem.* 59, 494 (1955).
2. Nicholson S., Shain I.: *Anal. Chem.* 36, 705 (1964).
3. Mareček V., Honz J.: *This Journal* 38, 487 (1973).

Translated by K. Míčka.