Analogue solution of kinetics of the disproportionation following a first-order chemical reaction

J. MOCÁK, D. I. BUSTIN, and V. PENCÁK

Department of Analytical Chemistry, Slovak Technical University,
880 37 Bratislava

Received 5 May 1976

Accepted for publication 30 September 1976

The disproportionation mechanism

$$O \xrightarrow{p} R$$

$$2R \xrightarrow{k} O+Z$$

in which both reactions take place in the bulk phase has been solved by means of an analogue computer. The first reaction can proceed as a chemical pseudomonomolecular redox reaction (excess of agent) or as an electrolytic first order reaction (at constant potential). The time profiles of the concentrations of all reaction components have been obtained. Several methods for the determination of rate constants by means of the working curves obtained by an analogue computer are proposed. The coulometric reduction of uranyl ions and the coulometric oxidation of chlorpromazine are given as examples of the application of the methods proposed for the study of the disproportionation kinetics.

Было осуществлено аналоговое решение механизма диспропорционирования

$$O \xrightarrow{p} R$$

$$2R \xrightarrow{k} O+Z$$

при котором обе реакции протекают во всем объеме раствора. Первая из реакций может протекать в виде химической, псевдомономолекулярной окислительно-восстановительной реакции (избыток реагента) или же как электролитическая реакция 1-го порядка (при постоянном потенциале). Были получены временные профили концентраций всех участвующих в реакции составляющих. Было предложено несколько способов определения констант скоростей при помощи рабочих кривых, полученных на аналоговой вычислительной машине. В качестве примера их применения для изучения кинетики диспропорционирования приводится кулонометрическое восстановление уранила и кулонометрическое окисление хлорпромазина.

One of the principal applications of computers (analogue as well as digital) in chemistry is their use for simulation of chemical processes [1, 2] (a comparison of digital and analogue computers in chemistry is presented in [3]).

This paper is concerned with the study of the disproportionation mechanism

$$\begin{tikzcd} \mathrm{O} \arrow[r, "p"] & \mathrm{R} & (1) \\ 2\mathrm{R} \arrow[r, "k"] & \mathrm{O}+\mathrm{Z} \arrow[ul] & (2) \end{tikzcd}$$

This mechanism was thoroughly studied and theoretical relationships were derived almost for all voltamperometric methods in the use of which reaction *(1)* took place on the working electrode with the rate constant p and the product of electrode reaction R underwent proper disproportionation reaction *(2)*. After the disproportionation mechanism had been solved by *Orlemann* and *Kern* [4] and *Koutecký* and *Koryta* [5] for polarography, the solutions were also obtained for single [6], current reversal [7], and cyclic [8] chronopotentiometry, single [9, 10] and "double-step" chronoamperometry [11], chronocoulometry [10], "linear-sweep" [12, 13] and cyclic voltammetry with symmetrical [14] and asymmetrical potential scan [15], "thin-layer" voltammetry [16], voltammetry with rotating electrode [17, 18], and A.-C. polarography [19]. As for coulometric methods, the solution was presented only for constant-current coulometry [20, 21]. Though the mechanism described by eqns *(1)* and *(2)* was also observed in controlled-potential coulometry, it has not been solved yet. The solution of this mechanism is the aim of this paper.

In contrast to voltamperometric methods, in coulometry reactions *(1)* and *(2)* take place in the bulk phase of solution. The formalism stated for coulometry is, therefore, identical with the formalism valid for the mechanism in which reaction *(1)* is a chemical first-order redox reaction.

Theory

Formulation of problem

If the reaction mechanism according to *(1)* and *(2)* is operating in the whole volume of solution, it may be described by a system of ordinary non-linear differential equations (in contrast to voltamperometric methods in which partial differential equations have to be used — their analogue solution is not preferable when compared with numerical calculation)

$$\frac{dc_1}{dt} = -pc_1 + 0.5\,kc_2^2 \tag{3}$$

$$\frac{dc_2}{dt} = pc_1 - kc_2^2 \tag{4}$$

$$\frac{dc_3}{dt} = 0.5\;kc_2^2 \tag{5}$$

The initial conditions are:

$$t = 0: \quad c_1(0) = c_1^0, \quad c_2(0) = c_3(0) = 0 \tag{6}$$

where c_1, c_2, and c_3 are concentrations of species O, R, and Z, respectively, t is time, and p and k are the rate constants of reactions (*1*) and (*2*), respectively. Introducing relative concentrations (referred to the initial concentration of the starting substance)

$$y_1 = \frac{c_1}{c_1^0}, \qquad y_2 = \frac{c_2}{c_1^0}, \qquad y_3 = \frac{c_3}{c_1^0} \tag{7}$$

the value of which is in the interval $\langle 0,1 \rangle$ it is possible to transform eqns (*3—5*) into more advantageous dimensionless form

$$\dot{y}_1 = \frac{dy_1}{dt} = -py_1 + 0.5\,kc_1^0\,y_2^2 \tag{8}$$

$$\dot{y}_2 = \frac{dy_2}{dt} = py_1 - kc_1^0\,y_2^2 \tag{9}$$

$$\dot{y}_3 = \frac{dy_3}{dt} = 0.5\;kc_1^0\,y_2^2 \tag{10}$$

$$t = 0: \quad y_1(0) = 1, \quad y_2(0) = y_3(0) = 0 \tag{11}$$

The introduction of dimensionless variables enables us to obtain the time dependence of c_1/c_1^0 from the solution of eqns (*8—11*) and, moreover, if the kinetics are experimentally investigated by controlled-potential coulometry, we can also obtain the time dependence of the relative value of electrolytic current i_t/i_0 because it holds [22]

$$\frac{c_1}{c_1^0} = \frac{i_t}{i_0} \tag{12}$$

where i_t is the instantaneous and i_0 the initial electrolytic current.

Analogue calculation

The analogue calculations were carried out on an analogue computer MEDA 40 AT (Aritma, Prague). The graphical record of the investigated functions was performed on an X—Y recorder BAK 4T (Aritma, Prague). The time axis of the recorder was controlled by the time base of the analogue computer. The general block diagram drawn in Fig. 1 belongs to eqns (*8—11*).

In order to solve the given system of differential equations by means of an analogue computer, it was necessary to make an amplitude normalization of all dependent variables and their derivatives lest the range ±1 MU should be exceeded at the output of a calculation unit (1 machine unit of a computer MEDA 40 AT is 10 V). Fig. 2 shows a detailed program diagram in which the amplitude normalization is respected. The fractions ahead of the symbols of integrators mean the gain of integrator $1/RC$ which can be achieved by a convenient ratio of the feedback- and input-resistance values of the integrator. According to the diagram presented in Fig. 2 the kinetics of disproportionation were solved for the value $p = 0.1\ \mathrm{s}^{-1}$ and various values of the "rate constant" $K = c_1^0 k$ ranging from 0.005 to $1.0\ \mathrm{s}^{-1}$. A general validity of the results obtained was ensured by introducing a dimensionless kinetic parameter

$$\varkappa = \frac{c_1^0 k}{p} = \frac{K}{p} \tag{13}$$

and a dimensionless time variable $pt = \tau$. Thus the results of the solution of disproportionation (time dependence of concentrations) are independent of the value of the rate constant p.

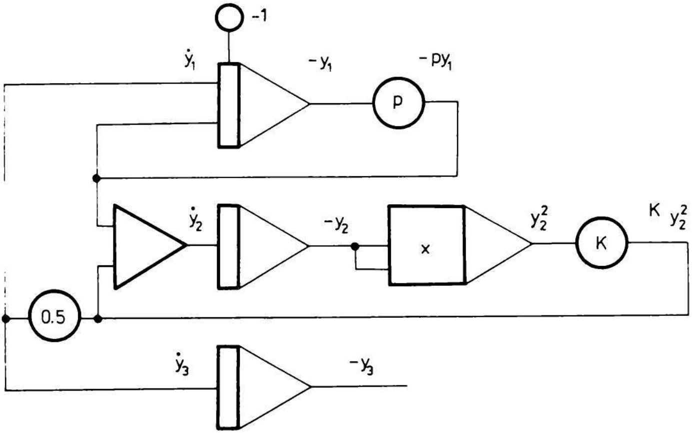


Fig. 1. Block diagram of the analogue solution for disproportionation of the product of a primary first-order reaction.

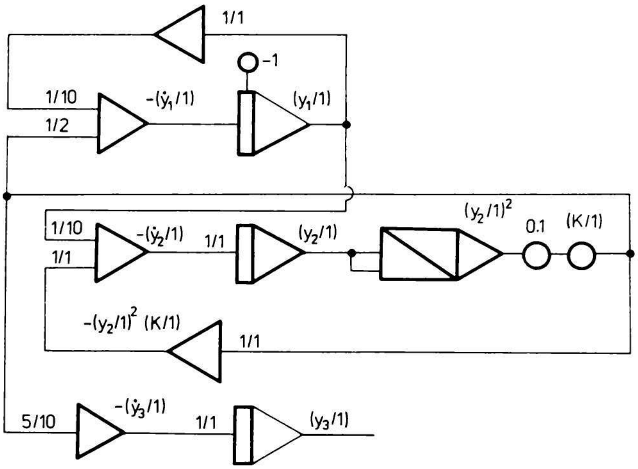


Fig. 2. Detailed analogue computer circuit diagram.

Experimental

Chemicals

All chemicals used were anal. grade preparations. Uranyl nitrate was prepared from a solution of 0.49 M-$NaClO_4$ and 0.01 M-$HClO_4$. The UO_2^{2+} solution was standardized by potentiometric dichromate titration of the U(IV) which was formed by previous reduction of the solution with $SnCl_2$ according to the method described by *Main* [23]. Before coulometric experiments the UO_2^{2+} solutions were carefully bubbled through with humidified nitrogen deoxygenated by passing through a solution of Cr(II) salt in the presence of zinc amalgame.

Apparatus

The coulometric measurements were performed by means of Universal Coulometric Analyzer OH-404 (Radelkis, Budapest). The time dependence of the electrolytic current was recorded on an X—Y recorder BAK 4T (Aritma, Prague) as the voltage drop on a calibrated 100-ohm resistor. The internal time base of the recorder served for the time measurement. The time axis and the potential axis of the recorder as well as the integrator of the analyzer OH-404 were calibrated separately.

The coulometric vessel was of cylindrical shape with two symmetrically placed compartments of auxiliary carbon electrodes which were separated from the working compartment by medium frits filled with agar gel. The auxiliary compartments contained an electrolyte consisting of 0.49 M-$NaClO_4$, 0.01 M-$HClO_4$, and 0.1 M hydrazine sulfate. The mercury bottom to which the end of a teflon stirrer reached (the free surface of the Hg electrode was 17.9 cm^2) was used as a working electrode. The teflon stirrer equipped with a wide thread reached into the vessel through a teflon head with holes for standard ground joints. A saturated calomel electrode connected with the investigated solution by means of a salt bridge was used as a reference electrode. The tip of the salt bridge was situated close to the surface of the working electrode on the spot where the highest current density was expected [24].

Before the reduction of the UO_2^{2+} ions the deoxygenated base electrolyte solution (40 ml $HClO_4$—$NaClO_4$, $I = 0.5$ M) was pre-electrolyzed at the same potential as it was in sample electrolysis (-0.35 V against SCE). The whole coulometric vessel was dipped into a thermostatic bath. All kinetic data given refer to the temperature 25°C.

Results and discussion

Time dependence of reaction components at different values of the kinetic parameter

The analogue solution gave the time profiles of relative concentrations of all the three reaction components for 20 different values of the parameter $\varkappa$. Some of them are presented in Figs. 3—5. Evidently, the concentration of the starting substance always decreases with time (Fig. 3) and the concentration of the final product increases monotonously (at the beginning of the reaction a certain induction period appears) exhibiting a point of inflection (Fig. 5). The concentration of intermediate increases initially, reaches a maximum and decreases afterwards (Fig. 4). These relationships are qualitatively similar to the concentration

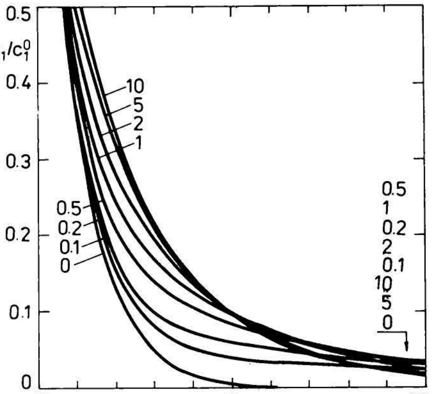


Fig. 3. Time profile of the concentration of the starting substance.
The values of the kinetic parameter $\varkappa$ are written at the curves.

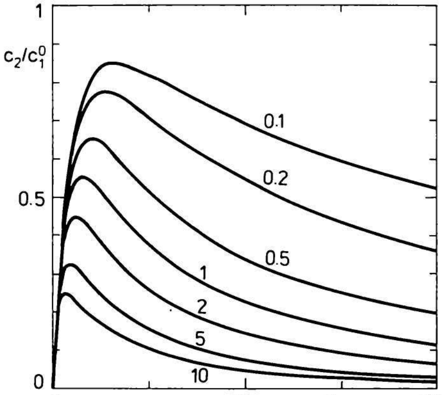


Fig. 4. Time profile of the concentration of the intermediate.
The values of $\varkappa$ are written at the curves.

profiles of the reaction components in a two-step consecutive reaction of the type $A \rightarrow B \rightarrow C$ (see [25]).

The accuracy of the values obtained by analogue solution may be easily checked by calculating the values of relative concentrations at any convenient time. As a matter of fact, the following equation follows from material balance

$$\frac{c_1}{c_1^0}+\frac{c_2}{c_1^0}+\frac{c_3}{c_1^0}=1 \tag{14}$$

In this way, it could be ascertained that the inaccuracy of the analogue solution increased with time and for $pt=18$ it attained $+2\%$—$+3\%$, *i.e*, the calculation according to eqn (*14*) gave the result between 1.02 and 1.03.

Determination of the rate constant of disproportionation

By using the working curves obtained by analogue technique the kinetic parameter $\varkappa$ may be determined from coulometric data by the following methods:

1. By comparing the experimental relationship between i_t/i_0 and pt with the working curves on the diagram in Fig. 3 and finding out the best fit (the ratio i_t/i_0 expresses the relative concentration of the starting substance, too — eqn (*12*)). For the determination of the "rate constant" K and for the calibration of the axis of abscisses in the units of dimensionless time variable pt the rate constant of electrolysis p must be known. Its value can be found out as the slope of the straight line section (at higher values of pt the relationship turns upwards) of the ln i_t *vs.* t plot, which represents the common method for the determination of the value of p in c.-p. coulometry [22].

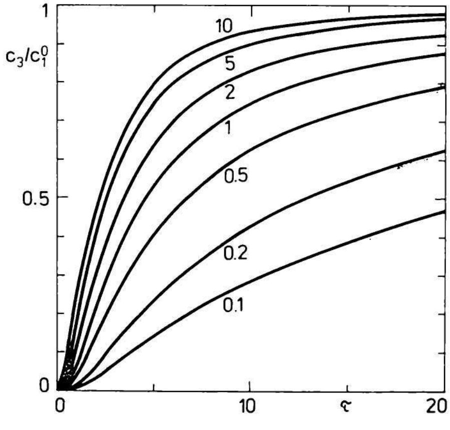


Fig. 5. Time profile of the concentration of the final product.
The values of $\varkappa$ are written at the curves.

2. By means of the diagram presented in Fig. 6 where the values of relative electrolytic current at different dimensionless time pt are plotted as a function of $\varkappa$. Besides the direct determination of the $\varkappa$ value, Fig. 6 also allows to estimate how the course of electrolytic current depends on the kinetic parameter $\varkappa$. It is obvious that the current changes very little with the value of $\varkappa$ at low values of pt. The influence of disproportionation manifests itself significantly only when $pt \geqslant 2.3$. In the absence of disproportionation ($\varkappa = 0$) this period of time corresponds to the time interval necessary for the electrolysis of 90% of the electroactive substance because $pt = \ln [100/(100 - P)]$ (where P denotes the percentage of electrolysis of the starting substance).

3. The kinetic parameter $\varkappa$ can be also determined by comparing the experimental plots c_2/c_1^0 *vs.* pt or c_3/c_1^0 *vs.* pt with the working curves presented in Fig. 4 or Fig. 5. To follow the time course of the concentration of intermediate or final product an arbitrary convenient analytical method (*e.g.* spectrophotometry) may be used. As the working curves presented in Figs. 3—5 were obtained on the assumption that the reaction mechanism described in terms of eqns (*1*) and (*2*) took place in the bulk phase of the solution, the first-order reaction (*1*) need not (but can) take place on electrode, but may proceed as an homogeneous redox reaction. The rate constant p of reaction (*1*) can be determined from the initial course of the plot $\ln [c_1/c_1^0]$ *vs.* t if the concentration of the starting substance is estimated by a convenient analytical method or from the course of electrolytic current, as described in point 1.

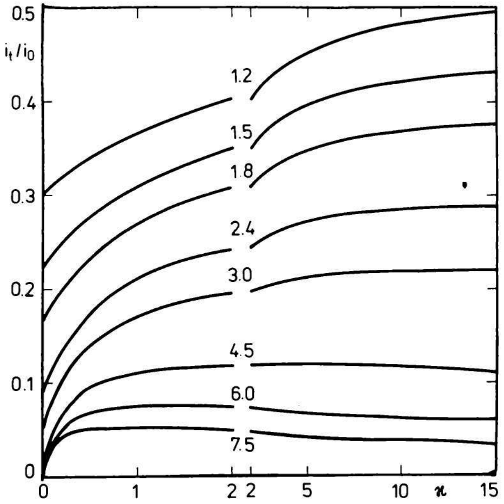


Fig. 6. Dependence of the relative electrolytic current on $\varkappa$ for different values of pt (written at the curves).

The time dependence of the intermediate changes with the value of $\varkappa$ most markedly (the height of maximum and its position) and for this reason the determination of $\varkappa$ on the basis of the concentration of intermediate may be considered to be the most accurate.

All the above methods for the determination of rate constants may be used even if the redox reaction (*1*) preceding disproportionation of the reaction product is oxidation.

Example of the determination of the rate constant K — disproportionation of the radical formed by oxidation of chlorpromazine

One-electron oxidation of the phenothiazine derivatives, which are important medicaments, gives rise to the radical identified by the e.s.r. method [26]. The coulometric investigation of the oxidation of chlorpromazine [27] showed a non-linear fall in the logarithm of electrolytic current with time, which indicated a complication in the electrode process by chemical reaction. On the basis of the course of electrolytic current found for oxidation in 1 N-H_2SO_4 which was presented in [27] we tried to confirm the disproportionation of the radical by the

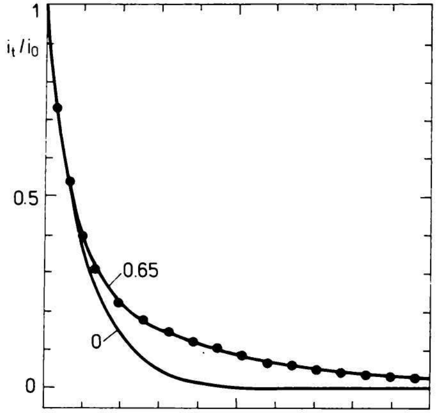


Fig. 7. Relative current as a function of time for the coulometric oxidation of chlorpromazine in 1 N-H_2SO_4 at + 1.0 V against SCE on a Pt-electrode.
Points – experimental values [27]; full lines – theoretical course (the values of $\varkappa$ are written at the curves).

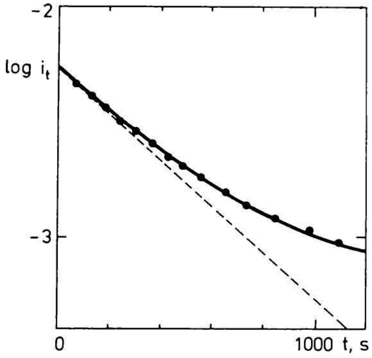


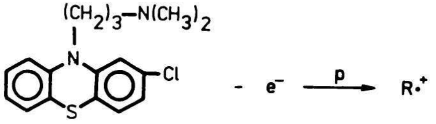
Fig. 8. Logarithm of the electrolytic current as a function of time for the reduction of 6×10^{-4} M-UO_2^{2+} in a $HClO_4$—$NaClO_4$ solution ($I = 0.5$ M) on a mercury macroelectrode. Concentration of the H^+ ions: $[H^+] = 1.48\times10^{-2}$ M; potential −0.35 V against SCE; speed of the stirrer 1000 r.p.m.
Points – experimental values; full line – theoretical course for $\varkappa = 0.5$; broken line – theoretical course for $\varkappa = 0$.

method of c.-p. coulometry and evaluate the rate constant of the disproportionation by means of the working curves (Fig. 3 or Fig. 6) according to the above-mentioned methods.

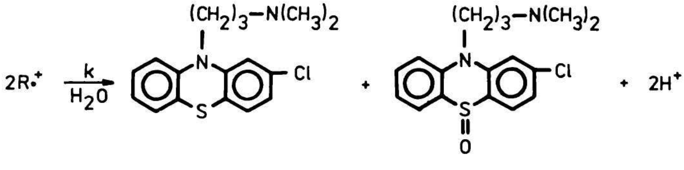
We determined the rate constant of electrolysis p directly from the slope of the graph log i *vs.* t. Then we transformed the values of electrolytic current and time into the coordinates i_t/i_0 and pt (Fig. 7). The experimental points are in good agreement with the theoretical working curve (Fig. 7).

Table 1 gives the results of the determination of K by the second method, *i.e.* by means of the working curves corresponding to the graph i_t/i_0 *vs.* $\varkappa$ for different values of pt. The average value of $\varkappa$ is in full agreement with the value of $\varkappa$ determined by the first method. By using the value of $\varkappa$ thus obtained and $p = 6.42 \times 10^{-3}\ \mathrm{s}^{-1}$ it was calculated according to eqn (*13*) that $K = 4.1 \times 10^{-3}\ \mathrm{s}^{-1}$ for the reaction in 1 N-H_2SO_4.

The good agreement of the experimentally found time dependence of electrolytic current with the working curve calculated for the disproportionation mechanism suggests the following pathway for the oxidation of chlorpromazine under coulometric conditions



(14)



(15)

Table 1

Determination of the kinetic parameter $\varkappa$ for disproportionation of the radical formed by oxidation of chlorpromazine

pt	i_t/i_0	$\varkappa$
2.1	0.212	0.68
2.4	0.187	0.62
2.7	0.168	0.62
3.0	0.153	0.63
4.5	0.103	0.70
	Average	0.65

Disproportionation of U(V) formed by the reduction of uranyl on a mercury electrode

The reduction of the uranyl cation was used as a model almost in all electrochemical methods [28, 29] to demonstrate the disproportionation mechanism (U(V) undergoes disproportionation to give U(IV) and uranyl). Fig. 8 represents the time dependence of the logarithm of electrolytic current which was observed in the coulometric reduction of UO_2^{2+} in slightly acidic solution. The initial values of this relationship were used for the determination of the rate constant of electrolysis $p = 2.51 \times 10^{-3}\ s^{-1}$ and the analogous relationship in Fig. 7 served for the determination of the kinetic parameter $\varkappa$. By using eqn (*13*) at a known initial concentration the rate constant of the disproportionation $k_{obs} = 1.91\ mol^{-1}\ l\ s^{-1}$ was calculated (by means of the working curves as in Fig. 3 or Fig. 6).

According to the mechanism originally proposed by *Kern* and *Orlemann* [30] a protonation equilibrium precedes the disproportionation and the observed rate constant depends linearly on concentration of the H^+ ions. By dividing the observed constant k_{obs} by the real concentration of the H^+ ions in solution a rate constant $k = 129\ mol^{-2}\ l^2\ s^{-1}$ independent of pH was obtained. The value of this constant is in relatively good agreement with the results obtained under similar conditions polarographically by *Koryta* and *Koutecký* [31] or with the results of kinetic measurements obtained by *Duke* and *Pinkerton* [32] who ascertained that $k_{obs}/[H^+] = 117\ mol^{-2}\ l^2\ s^{-1}$ in 0.5 M-$NaClO_4$—$HClO_4$. A comparison with the data published in [33] gives a still better agreement. Here the results of different authors are plotted in the coordinates log k *vs.* $I^{1/2}$. The value of $k = 126\ mol^{-2}\ l^2\ s^{-1}$ corresponds to the ionic strength of $I = 0.5$ M in perchlorate solution.

The detailed studies [28, 29] have shown that the mechanism of the disproportionation of uranyl depends on the pH interval in which the reaction sequence is investigated, on ionic strength, character of anion as well as the concentration of uranyl while alternative reactions may be operative: ECE mechanism [28] or formation of a binuclear complex $U_2O_4^{3+}$ [34]. A more detailed study of disproportionation of U(V) by the use of c.-p. coulometry in slightly acidic medium will be the topic of our next paper [35].

References

1. Janata, J. and Mark, H. B., Jr., *Application of Controlled-Current Coulometry to Reaction Kinetics*, in A. J. Bard (Editor), *Electroanalytical Chemistry*, Vol. *3*. Marcel Dekker, New York, 1969.
2. Mark, H. B., Jr., *Basic Principles of the Electronic Analog Computer*, in J. S. Mattson, H. B. Mark, Jr., H. C. MacDonald, Jr. (Editors), *Computer Fundamentals for Chemists*. Marcel Dekker, New York, 1973.
3. Sellers, J. G., *Analog Response by Digital Computers*, in J. S. Mattson, H. B. Mark, Jr., H. C.

MacDonald, Jr. (Editors), *Computer Fundamentals for Chemists.* Marcel Dekker, New York, 1973.

4. Orlemann, E. F. and Kern, D. M. H., *J. Amer. Chem. Soc.* ***75,*** 3058 (1953).
5. Koutecký, J. and Koryta, J., *Collect. Czech. Chem. Commun.* ***20,*** 845 (1953).
6. Fischer, O. and Dračka, O., *Collect. Czech. Chem. Commun.* ***24,*** 3046 (1959).
7. Feldberg, S. W. and Auerbach, C., *Anal. Chem.* ***36,*** 505 (1964).
8. Čukman, D. and Pravdič, V., *J. Electroanal. Chem.* ***49,*** 415 (1974).
9. Booman, G. L. and Pence, D. T., *Anal. Chem.* ***37,*** 1366 (1965).
10. Feldberg, S. W., *J. Phys. Chem.* ***73,*** 1238 (1969).
11. Marcoux, L., *J. Phys. Chem.* ***76,*** 3254 (1972).
12. Mastrogostino, M., Nadjo, L., and Saveant, J. M., *Electrochim. Acta* ***13,*** 721 (1968).
13. Nadjo, L. and Saveant, J. M., *J. Electroanal. Chem.* ***33,*** 419 (1971).
14. Olmstead, M. L. and Nicholson, R. S., *Anal. Chem.* ***41,*** 862 (1969).
15. Nadjo, L. and Saveant, J. M., *Electrochim. Acta* ***16,*** 887 (1971).
16. McDuffie, B. and Reilley, C. N., *Anal. Chem.* ***38,*** 1881 (1966).
17. Ulstrup, J., *Electrochim. Acta* ***13,*** 1717 (1968).
18. Holub, K., *J. Electroanal. Chem.* ***30,*** 71 (1971).
19. Breyer, B., Beevers, J. R., and Bauer, H. H., *J. Electroanal. Chem.* ***2,*** 60 (1961).
20. Cover, R. E. and Meites, L., *J. Phys. Chem.* ***67,*** 2311 (1963).
21. Kastening, B., *Collect. Czech. Chem. Commun.* ***30,*** 4033 (1965).
22. Lingane, J. J., *J. Amer. Chem. Soc.* ***67,*** 1916 (1945).
23. Main, A. R., *Anal. Chem.* ***26,*** 1507 (1954); Kolthoff, I. M., Belcher, R., Stenger, V. A., and Matsuyama, G., *Volumetric Analysis,* Vol. *3.* (Russian Ed.) Goschimizdat, Moscow, 1961.
24. Harrar, J. E. and Shain, J., *Anal. Chem.* ***38,*** 1148 (1966).
25. Frost, A. A. and Pearson, R. G., *Kinetics and Mechanism,* 2nd Ed. Wiley, New York, 1965.
26. Piette, L. H., Ludwig, P., and Adams, R. N., *Anal. Chem.* ***34,*** 916 (1962).
27. Merkle, F. H. and Discher, C. A., *Anal. Chem.* ***36,*** 1639 (1964).
28. Mastragostino, M. and Saveant, J. M., *Electrochim. Acta* ***13,*** 751 (1968).
29. Čukman, D., Vukovič, M., and Pravdič, V., *J. Electroanal. Chem.* ***49,*** 421 (1974).
30. Kern, D. M. H. and Orlemann, E. F., *J. Amer. Chem. Soc.* ***71,*** 2102 (1949).
31. Koryta, J. and Koutecký, J., *Collect. Czech. Chem. Commun.* ***20,*** 423 (1955).
32. Duke, F. R. and Pinkerton, R. C., *J. Amer. Chem. Soc.* ***73,*** 2361 (1951).
33. Masters, J. and Schwartz, L. L., *J. Amer. Chem. Soc.* ***83,*** 2620 (1961).
34. Newton, T. W. and Baker, F. B., *Inorg. Chem.* ***4,*** 1166 (1965).
35. Mocák, J. and Bustin, D. I., *J. Electroanal. Chem.* ***79***, 307 (1977).

Translated by R. Domanský