DATA PROCESSING IN REACTION RATE MEASUREMENTS FOLLOWED AMPEROMETRICALLY

A.TROJÁNEK and R.KALVODA

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 118 40 Prague 1*

For semiautomatic measurement of the rate of chemical reactions of first (or pseudo first) order, an analogue circuit was constructed, which is fed with the current from an indicator electrode in a potentiostatic circuit. The apparatus was used in measuring the kinetics of the reaction of acetone with ferricyanide in alkaline medium.

In measurements of the rates of chemical reactions, usually the slope, *i.e.* the time derivative of a signal from a detector sensitive to changes of concentration of a reagent is determined. More complicated circuits enable even to determine directly the reaction rate constant[1−4]. The amperometric method can be conveniently used[5−8] in measuring the concentration changes of electroactive compounds reacting in solution since the current depends linearly on concentration in a wide range. A simple record of *i–t* curves of a substance formed or consumed during the reaction enables to calculate the kinetic parameters either from the reaction half-time or from the initial reaction rate.

The subject of the present work is an electronic treatment of the current signal in controlled-potential electrolysis enabling to follow the total reaction course with exclusion of the rather inaccurate evaluation of graphical records.

THEORETICAL

In the case of a reaction of first (or pseudo first) order, $A \rightarrow B$, the concentrations of the starting substance and product change with time according to

$$C_A = C_A^0 e^{-kt}, \qquad C_B = C_A^0(1 - e^{-kt}), \qquad (1), (2)$$

where C_A^0 denotes initial concentration of A (that of B is assumed to be zero). With electrochemical *i.e.* amperometric measurements, the concentrations can be replaced by limiting currents to obtain

$$i_A = i_A^0 e^{-kt}, \qquad i_B = i_B^M(1 - e^{-kt}), \qquad (3), (4)$$

where i_B^M denotes maximum limiting current of B. These equations are obviously valid also in the case where the proportionality constants in the relations $i_A = K_1 C_A$ and $i_B = K_2 C_B$ are different.

The rate constant, k, can be evaluated from Eq. (3) simply with the aid of an analogue logarithmic module (Fig. 1, on top). If the concentration of the product B is followed, a derivative module must be added into the circuit (Fig. 1, on bottom). Thus, linear functions are obtained, from which the k values can be simply calculated or, if another derivative module is added, read directly on a scale.

EXPERIMENTAL

Treatment of Signal According to Fig. 1a

To follow the concentration of the starting substance, the circuit shown in Fig. 2 was used. Operational amplifiers Z1 and Z2 together with electrolytic vessel EL form a potentiostat for electrolysis at controlled potential. The signal from the indicator electrode is fed to a circuit formed by a current follower, an active filter and a logarithmic module. The current follower of common type is supplemented by a circuit for compensation of the residual current of supporting electrolyte by a voltage applied on the summing resistance, R_s. The compensation voltage is taken from a twenty-revolution potentiometer of the type Aripot 35120 connected to a source of 1·5 V reference voltage. This compensation is inevitable to avoid distortion of the resulting function on the output of the logarithmic module. The active filter of Butterworth type with an upper cut-off frequency of 1·1 c.p.s. eliminates current fluctuations which would interfere in cases where the signal is weak (*i.e.* when the logarithmic module operates in the steep part of the logarithmic
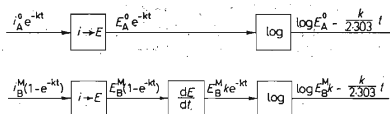

Fig. 1
Basic Circuits for Treatment of Signal During Following the Starting Substance (A) or the Product (B)
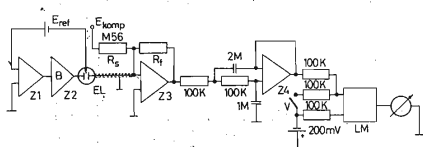

Fig. 2
Circuit for Obtaining and Treatment of *i–t* Curve of the Starting Substance
    Amplifiers: Z1, Z3 AS 101; Z2 Analog Devices B-100; Z4 Teledyne Philbrick 1009; LM logarithmic module Teledyne Philbrick.

function). The logarithmic circuit consists of two operational amplifiers with FET transistors on the input which are connected to a Teledyne Philbrick 4358 module consisting in substance of two transistors connected to the feedback of the operational amplifiers. The output signal from the logarithmic module is given by $E_0 = -K \log (E_1 R_2/E_2 R_1)$, where $K = 1.000$ V, $R_1 = R_2 = 100$ kΩ. A constant voltage of 200 mV is applied to the input E_1. A switch, V, serves to prevent the logarithmic module from driving to saturation in the case when the signal on the input E_2 is equal to zero; it is disconnected during measurement. The signal on the output of the logarithmic module is recorded by Electronic Polyrecorder EPR-2 TC (Toa Electronics, Tokyo).

Treatment of Signal According to Fig. 1b

To follow the concentration of the product, the circuit shown in Fig. 3 was used. The signal from the indicator electrode connected to the potentiostat built from operational amplifiers Z1 and Z2 is fed to a circuit formed by a current follower, filter 1, derivative module, filter 2 and logarithmic module. Active filters 1 and 2 of Butterworth type have their upper cut-off frequencies of $5.6 . 10^{-3}$ and 1.2 c.p.s. With respect to the derivative module in the circuit, a very low cut-off frequency of the first filter had to be chosen. When an experimental course was simulated by an analogue signal the course of the signal on the current follower output was identical with that on the output of the filter F1. This experiment proved that the distortion of the signal by the filter was negligible. The output signal from the derivative module passed through the filter F2. In view of the high impedance of F1, an amplifier with FET transistors on its input was used.

A suitable choice of the feedback resistance R_F in the current follower and of the R_d and C_d values in the derivative module ensures optimum utilization of the operational units, $i.e.$ attainment of maximum output signal of the derivative module (up to 10 V). For maximum output voltage of the derivative module, the relation $E_d^M = R_F \, i_B^M R_d C_d k$ applies; to choose correctly the values of R_d and C_d (for a given value of R_F for the current follower), the value of k must be known roughly; it can be estimated, $e.g.$, from the reaction half-time after an i–t curve is
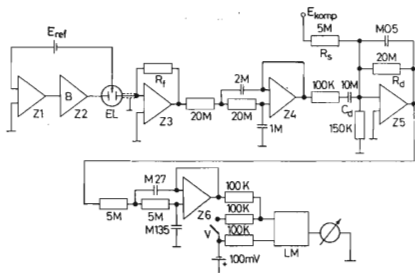

FIG. 3

Circuit for Obtaining and Treatment of i–t Curve of the Reaction Product

Amplifiers: Z1, Z3 AS 101; Z2 Analog Devices B-100; Z4 Teledyne Philbrick 1009; Z5 Analog Devices 118 A; Z6 Fairchild AD 044. LM Logarithmic module Teledyne Philbrick.

recorded. Also in this circuit, any undesirable signals must be compensated. The compensating voltage is in this case fed to the summing point of the operational amplifier connected as a derivative module in a similar manner as in Fig. 2. The logarithmic module is designed analogously as in the preceding case.

Testing the Apparatus by an Analogue Signal

The circuits in Figs 2 and 3 were tested with signals generated by a simple analogue circuit (Fig. 4). Its left half consists of an operational amplifier connected as an integrator which solves the differential equation $dx/dt = -kx$ with the initial condition $t = 0$, $x = x_0$. Hence, the signal on its output simulates the time course of the concentration of A. The right half consists of an adder whose output signal simulates the time course of the concentration of B. Switch P serves to introduce the initial x_0 value (position 1); to obtain the solution, it is set to position 2. The values of k are set by an Aripot type helicoidal potentiometer. In testing the circuit shown in Fig. 2, the slopes of straight lines obtained by logarithming the output signal of the integrator were compared with the slopes of straight lines obtained by logarithming the same signal passed through the filter. In testing the circuit shown in Fig. 3, the slopes of straight lines obtained by
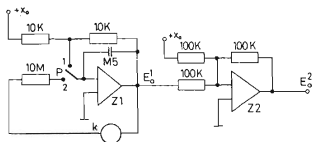

FIG. 4

Generator for Simulation of Kinetic i–t Curves

Z1 AS 101; Z2 Analog Devices 1055. $E_0^1 = -x_0 \exp(-kt/5)$; $E_0^2 = -x_0[1 - \exp(kt/5)]$.
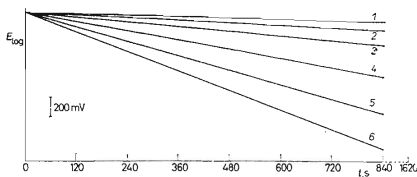

FIG. 5

Output Signal of the Circuit from Fig. 2

Electrode rotation speed 1100 r.p.m., $R_F = 2.5$ MΩ. Initial concentration of ferricyanide in 1.05M-KOH $1 . 10^{-4}$M. Concentration of acetone: 1 $2 . 10^{-3}$M; 2 $5 . 10^{-3}$M; 3 0.01M; 4 0.02M; 5 0.03M; 6 0.04M.

logarithming the output signal of the integrator were compared with the slopes of straight lines on the output of the logarithmic module after the signal from the adder passed through the whole circuit. In the range $0.01 \leqq k \leqq 0.2$, the error did not exceed 5%.

Oxidation of Acetone with Ferricyanide in Alkaline Medium

The usefullness of the described apparatus was verified in following the reaction of acetone with ferricyanide in 1.05M-KOH. This reaction is not a simple one as evidenced by kinetic measurements during constant-potential electrolysis on an electrode with a large surface[9]. At a large excess of acetone and KOH in a closed system the reaction is of pseudo first order. The constant k in Eqs (4) and (3) is then a function of the concentration of OH^- ions and acetone.

Electrolytic vessel and electrodes. Measurements were made in an opened cylindrical electrolytic glass vessel of 80 ml holding capacity provided with a thermostated mantle. The reaction volume was 55 ml. The amperometric circuit consisted of a potentiostat and electrodes. The indicator electrode was a rotating platinum disc, 3 mm in diameter. The minimum speed of rotation ensuring a sufficiently quick mixing of the reagents was about 1 000 r.p.m. (Although a stationary platinum wire electrode with a rotating stirrer performed also satisfactorily, the rotating electrode was preferred since it eliminated considerably the fluctuations of current, which interfere with the measurement especially when a derivative module with a higher time constant is used, such as $RC = 200$ s in our case. At any rate, filters must be employed in the circuit.) The reference electrode was s.c.e. and the counter electrode a graphite rod separated from the reaction compartment by a sintered glass diaphragm.

Chemicals. Stock solutions of 10M-KOH, 0.01M ferro- or ferricyanide and 1M acetone were prepared from reagent grade chemicals.

Method of measurement. The potential of the indicator electrode was $+50$ or $+400$ mV (s.c.e.) according to whether the ferri- or ferrocyanide concentration was followed (values based on a recorded voltammetric curve). The method of measurement was essentially the same in either case. At the preset voltage of 50 mV, the residual current of the KOH solution at 25°C
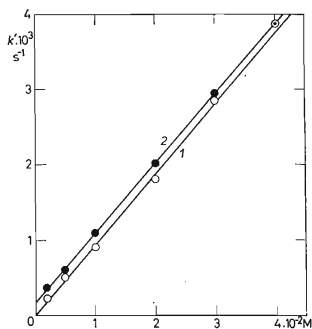

Fig. 6

Dependence of Slopes of Straight Lines from Fig. 5 (1) and of Linear Parts from Fig. 7 (2) on Concentration of Acetone

was compensated to obtain zero signal on the filter output, ferricyanide was added and the auxiliary voltage on the input of the logarithmic module was switched off by switch V (Fig. 2). After a short time the output signal of the logarithmic amplifier became constant, the pen recorder chart was set in motion and acetone added either by a pipette or from a teflon dish, which made no difference owing to the slowness of the reaction (when the ferrocyanide concentration was followed, the initial steep course was damped by the filters, cf. Fig. 7).

RESULTS AND DISCUSSION

The transformed experimental $i–t$ curves are shown in Fig. 5. From the dependence of the slope of these lines on the concentration of acetone (Fig. 6, *1*) it follows that the reaction is of first order with respect to acetone in the concentration range considered. The slope of the straight line corresponds to $9\cdot4 . 10^{-2} \, l \, mol^{-1} \, s^{-1}$. This value is in good agreement with the constant of the reaction of pseudo second order measured[9] in 1M-KOH by the steady state method in electrolysis with an electrode of large surface area, namely $8\cdot5 . 10^{-2} \, l \, mol^{-1} \, s^{-1}$.

When the circuit according to Fig. 3 was used it was necessary to wait for a few minutes after the addition of ferricyanide until the output signal of the second filter became constant and to compensate it if necessary. The recorder chart was set in motion and several seconds after addition of acetone the auxiliary voltage on the input E_2 of the logarithmic module was switched off by switch V. The recorded curves are shown in Fig. 7. The dependence of the slope of the linear part of these curves on the concentration of acetone is again linear with a slope of $9\cdot3 . 10^{-2} \, l \, mol^{-1} \, s^{-1}$ (Fig. 6, *2*) in good agreement with the above result although this straight line does not pass through the origin of coordinates. This anomaly may be caused by the state of the electrode surface at the applied potential and obviously has nothing in common
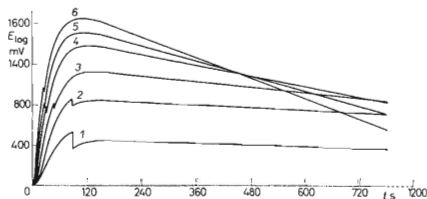

FIG. 7

Output Signal of the Circuit from Fig. 3

Electrode rotation speed 1100 r.p.m., R_F 2·5 MΩ. Initial concentrations of acetone for curves *1—6* are the same as in Fig. 5. (The discontinuity on the rising portion of the curves is due to switching off of the auxiliary source from the logarithmic module.)

with the course of the chemical reaction (Fig. 6 and results of voltammetric measurements in ref.[9]) or with the apparatus, which was carefully tested. The rate constants obtained in the present work were compared with those derived from electrolysis at constant potential by the method described previously[10,11] as well as by the classical method, in which the voltammetric curves of the reaction mixture were recorded at certain time intervals. From the measured cathodic and anodic currents the dependences of log i_k and log $(i_a^M - i_a)$ on t were plotted, where the value of i_a^M was found by extrapolating the dependence of i_a on t (Eq. (4)). A plot of k against concentration of acetone gave straight lines passing through the origin of coordinates with a slope of $9 . 10^{-2} \, \mathrm{l \, mol^{-1} \, s^{-1}}$ (from the cathodic current) or $9 \cdot 2 . 10^{-2} \, \mathrm{l \, mol^{-1} \, s^{-1}}$ (from the anodic current). This is in good agreement with the above results. However, the advantage of the semiautomatic method consists in a more rapid work and simplified handling. The proposed electric circuits can be modified for more rapid reactions (a change of the frequency characteristics of the filters) assuming rapid mixing of reaction components.

The described apparatus can be used also in semiautomatic kinetic measurements in analytical chemistry enabling to utilize analytically a number of reactions that are not suitable for usual analytical measurements performed normally in equilibrium systems. These are, *e.g.*, reactions attaining equilibrium very slowly, systems with parallel reactions proceeding to the end or those which do not proceed quantitatively. The substance in question can be determined by measuring the rate of its reaction with a suitable reagent. Since the theory of analyses based on second-order reactions is complicated it is preferable to choose the experimental conditions such that the reaction becomes a pseudo first-order one. To this purpose the concentration of the substance to be determined should be about 50 times the initial concentration of the reagent[12].

In our case, where the recorded output signal of the circuit shown in Fig. 2 or 3 gives a straight line with a slope of $k' = k_s[Z]$ (Fig. 6), it is possible even without preceding calibration to determine the concentration, Z_x, of the component present in a relative excess by the method of standard addition, Z_0. The slopes k'_1 and k'_2 measured for the concentration before (Z_x) and after addition $(Z_x + Z_0)$ are given by $k'_1 = k_s Z_x$ and $k'_2 = k_s(Z_x + Z_0)$, whence $Z_x = Z_0 k'_1/(k'_2 - k'_1)$. The design of an apparatus for kinetic measurements in analytical chemistry will be the subject of a later communication.

REFERENCES

1. Cordos E. M., Drouch S. R., Malmstadt H. V.: Anal. Chem. *40*, 1812 (1968).
2. James G. E., Pardue H. L.: Anal. Chem. *40*, 796 (1968).
3. Weichselbaum T. E., Plumpe W. H., jr. Adams R. E., Hagerty J. C., Mark H. B., jr.: Anal. Chem. *41*, 725 (1969).
4. Pardue H. L., Dahl W. E.: J. Electroanal. Chem. *8*, 268 (1964).

5. Kolthoff I. M., Reynolds W. L.: Discussions Faraday Soc. *17*, 1967 (1954).
6. Rosseinsky D. R., Nicol M. J.: Electrochim. Acta *11*, 1069 (1966).
7. Rosseinsky D. R., Nicol M. J.: Trans. Faraday Soc. *64*, 2410 (1968).
8. Němec I., Kies H. L., Němcová I.: Anal. Chim. Acta *49*, 541 (1970).
9. Trojánek A.: *Thesis*. Charles University, Prague 1970.
10. Kalvoda R.: J. Electroanal. Chem. *24*, 53 (1970).
11. Rechnitz G. A., McClure J. E.: Anal. Chem. *36*, 2265 (1964).
12. Mark H. B., jr., Rechnitz G. A., Grienke R. A.: *Kinetics in Analytical Chemistry*. Interscience, New York 1968.

Translated by K. Micka.