DETERMINATION OF RATE CONSTANTS OF REDOX REACTIONS OF SECOND ORDER FROM CURRENT-LESS POTENTIAL-TIME CURVES BY A SIMPLIFIED GRAPHICAL-NUMERICAL METHOD*

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Received September 30th, 1981

A method for constructing curves is proposed that are linear in a wide region and from whose slopes it is possible to determine the rate constant, if a parameter, θ, is calculated numerically from a rapidly converging recurrent formula or from its explicit form. The values of rate constants and parameter θ thus simply found are compared with those found by an optimization algorithm on a computer; the deviations do not exceed $\pm 10\%$.

One of our preceding communications[1] dealt with the method how to determine the rate constant of a second-order redox reaction $z_1\,\mathrm{Ox}_2 + z_2\,\mathrm{Red}_1 \xrightarrow{k_1} z_1\,\mathrm{Red}_2 + z_2\,\mathrm{Ox}_1$ from a set of non-equilibrium potential-time (E–t) curves at a molar ratio of the starting compounds $n = z_2\,.\,[\mathrm{Ox}_2(t = 0)]/z_1[\mathrm{Red}_1(t = 0)]$ as parameter, and this even in the case where the indicator electrode does not behave ideally. The method was based on plotting the quantity $t(1 - n)$ against $\mathfrak{Z}$ (Eq. ($1a_2$) in ref.[1]), whereby either a straight line was obtained (with an ideal electrode) or a curve with a "beak", a sign of nonideality of the electrode. The slope of the descending, practically linear portion of the beak-like curve gave the rate constant; the ratio, θ, of the slopes of the ascending and descending portions of the beak-like curve enabled us to linearize this curve as a whole and from the resulting slope, in turn, to determine the rate constant k_1. This procedure, however, can be used only if the dependence of $t(1 - n)$ on $\ln n$, obtained from the experimental E–t curves with the aid of the lines $E =$ const., has an extremum.

The other type of the $t(1 - n) - \ln n$ dependence is monotonous and has a vertical asymptote[2]. In this case, no method was found how to recognize the nonideality of the electrode and to determine the rate constant k_1.

The present work deals with a simplified method for the determination of the rate constant of second-order redox reactions from E–t curves recorded with a nonideal electrode, and this for any type of the experimental $t(1 - n) - \ln n$ curves.

THEORETICAL

As shown earlier[1], the quantity $\tau(1 - n)$ fulfils the equation

$$\tau(1 - n) = \ln\left[(n^{\theta}(1 - n) + Dn^{\theta})/(\beta(1 - n) + Dn^{0})\right], \qquad (1)$$

* Part XVIII in the series Application of Potential–Time Curves in Reaction Kinetics; Part XVII: This Journal *46*, 561 (1981).

where for an ideal electrode $\theta = 1$, for a nonideal one $\theta \neq 1$, and $\tau = k_1 z_1[\mathrm{Red}_1 \,.\, (t = 0)]\, t$. For $D > 0$, the $\tau(1 - n) - \ln n$ curves have an extremum (and the above-mentioned method for the determination of k_1 could be used), for $D < 0$ they have a curvature towards a vertical asymptote, and for $\beta = 0$ they form a descending arc.

Curves for $D > 0$

The new method will be illustrated first on the $t(1 - n) - \ln n$ curves for $D > 0$ (with an extremum) and $\theta = 1$. If the curve according to Eq. (*1*) is intersected with a horizontal line $t(1 - n) \equiv \bar{y} = \text{const.}$, we obtain a quadratic equation for n with roots n_1 and n_2

$$n^2 + n(e^y(D - \beta) - D - 1) + e^y\beta = 0\,; \quad y = \bar{y} z_1 k_1[\mathrm{Red}_1(t = 0)]\,, \qquad (2a)$$

whose product $n_1 n_2 = e^y\beta$. Let us call the values of $\ln n_1$ and $\ln n_2$ a conjugated pair. Since

$$\ln n_1 + \ln n_2 = y + \ln \beta\,, \qquad (2b)$$

by plotting the sum of the conjugated pair against chosen values of $t(1 - n) = \bar{y}$ we obtain a straight line (Fig. 1) which delimits the value of $\ln \beta$ on the abscissa and whose slope is $(k_1 z_1[\mathrm{Red}_1(t = 0)])^{-1}$. This value enables us to calculate the rate constant k_1.

Otherwise, Eq. (*2b*) with a chosen value of n_1 can be interpreted on the basis of Eq. (*1*) (after a simple rearrangement) so that

$$y + \ln \beta = \ln \frac{n_1(1 - n_1) + Dn_1}{1 - n_1 + n_1 D/\beta} = \ln (n_1 n_2)\,. \qquad (2c)$$

Hence, the right-hand side of Eq. (*1*) is in this way decomposed to the product of $n_1 n_2$, and obviously

$$n_2 = (1 - n_1 + D)/(1 - n_1 + n_1 D/\beta)\,. \qquad (2d)$$

Actually, this is an expression for n_2 as a function of n_1 (compare the expression for the absolute term of a quadratic equation) assuming $\theta = 1$. Also, Eq. (*2d*) is a definition of the conjugated pair n_1 and n_2 for $\theta = 1$.

Now, the question is whether the sum of the conjugated pair $\ln n_1 + \ln n_2$ can be made use of in the case of a nonideal electrode, *i.e.*, for $\theta \neq 1$. In this case, an analogue of Eq. (*2c*) based on Eq. (*1*) can be written as

$$y + \ln \beta = \ln \frac{n_1^\theta(1 - n_1) + Dn_1^\theta}{1 - n_1 + n_1^\theta D/\beta} = \ln (n_1^\theta n_2^\theta) = \theta(\ln n_1 + \ln n_2)\,. \qquad (3a)$$

For n_2 conjugated to a chosen value of n_1 we now have

$$n_2^\theta = (1 - n_1 + D)/(1 - n_1 + n_1^\theta D/\beta) \tag{3b}$$

and, generally, the value of n_2 need not be on the curve $\tau(1 - n) - \ln n$ for a chosen level $\tau(1 - n) = y$, since the corresponding equation for n at a fixed y reads

$$n^{\theta+1} - n^\theta(1 + D - e^y D) - ne^y\beta + e^y\beta = 0 \tag{3c}$$

and the product of $(n_1 n_2)^\theta = \beta e^y$ is generally different from the product of the roots of Eq. (*3c*).

For constructing the straight line $y + \ln \beta = \theta(\ln n_1 + \ln n_2)$, two points must be known, *i.e.*, two conjugated pairs $\ln n_1^{(1)}$, $\ln n_2^{(1)}$ and $\ln n_1^{(2)}$, $\ln n_2^{(2)}$. The first one is obtained from Eq. (*3b*) by setting $n_1^{(1)} = 1$, whence $n_2^{(1)} = \beta^{1/\theta} = n(t = 0)$, which is identical with one of the values of n following from Eq. (*1*) for $t = 0$. The first conjugated pair is thus formed by the points of the $t(1 - n) - \ln n$ dependence lying on the axis of abscissae.

Finding additional conjugated pairs for different values of n_1 according to Eq. (*3b*) requires the knowledge of the parameters D, β, and θ, which, however, cannot be

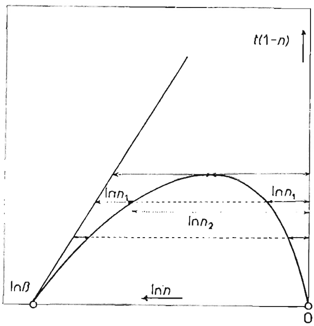

FIG. 1

Dependence of $t(1 - n)$ on $\ln n$ and construction of the tangent in the left limiting point. Parameters: $\theta = 1$, $D > 0$, $\beta \neq 0$

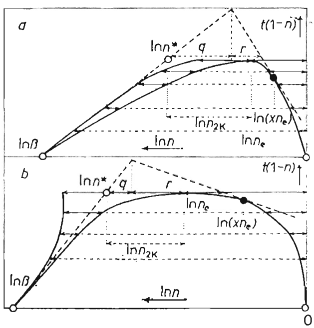

FIG. 2

Dependence of $t(1 - n)$ on $\ln n$ for a non-ideal electrode. Parameters: *a*) $D > 0$, $\theta < 1$, $\beta \neq 0$; *b*) $D < 0$, $\theta > 1$, $\beta \neq 0$. Geometric check: $\theta = r/q$

directly obtained from the experimental $t(1-n) - \ln n$ curves. Nevertheless, on the level $t(1-n) = \bar{y}_e$ corresponding to the extremum of the $t(1-n) - \ln n$ curve, *i.e.*, for $n_1 - n_e$ it is possible to find another conjugated pair from the condition of extremum of the function (*1*)

$$\frac{d\tau(1-n)}{d \ln n} = \theta - \frac{n}{1-n+D} - \frac{Dn^0 - \beta n}{\beta(1-n) + Dn^0} = 0\,. \qquad (4a)$$

Its sum, $\ln n_1^{(2)} + \ln n_2^{(2)}$, is given by the abscissa, $\ln n$, corresponding to the intersection of the horizontal, $\bar{y}_e$, with the tangent of the $t(1-n) - \ln n$ curve in the point $n = \beta^{1/\theta}$, *i.e.*, in the point $n(t=0)$, hence with the tangent drawn in the left limiting point of the $t(1-n) - \ln n$ curve on the axis of abscissae.

The slope of this tangent is according to Eqs (*1*) and (*4a*) given as

$$\left(\frac{d\tau(1-n)}{d \ln n}\right)_{n=\beta^{1/\theta}} = \theta \frac{1-\beta^{1/\theta}}{1-\beta^{1/\theta}+D}\,. \qquad (4b)$$

For usual values[2] of $D \ll 1 - n$, this equation is simplified and leads to the equation of the tangent

$$\tau(1-n) = \theta \ln n - \ln \beta\,. \qquad (4c)$$

For the horizontal line, $y_e = \tau(1-n_e)$, led through the extremum point we have according to Eq. (*3a*)

$$\tau(1-n_e) = \theta \ln (n_e n_2) - \ln \beta\,, \qquad (4d)$$

and its point of intersection with the tangent is given as

$$\ln n^* = \ln n_e + \ln n_2\,. \qquad (4e)$$

Based on Eq. (*4a*) for $D \ll 1 - n_e$, the following equation results

$$D/\beta = \theta(1-n_e)^2/\{n_e^{\theta+1} - [n_e + (1-n_e)\,\theta]\, n(t=0)^\theta\} \approx \theta(1-n_e)^2/n_e^{\theta+1}\,. \qquad (4f)$$

Hence, the value of n_2 conjugated to n_e is on the basis of Eq. (*3b*) given as

$$n_2^\theta = (1-n_e)/[1-n_e+\theta(1-n_e)^2/n_e] = n_e/[n_e+\theta(1-n_e)]\,. \qquad (4g)$$

For an ideal electrode, $\theta = 1$ and according to Eq. (*4g*) $n_2 = n_e$; for a nonideal one, either $\theta < 1$ and $n_2 < n_e$ or $\theta > 1$ and $n_2 > n_e$ as follows from Eq. (*4g*) (Fig. 2).

The geometric interpretation is as follows. When the $t(1-n) - \ln n$ dependences are treated in the same way as for $\theta = 1$, *i.e.*, when the sums, $\ln n_1 + \ln n_2$, of the abscissae of both points of these curves on the chosen horizontals $t(1-n) = \bar{y} =$ = const. are plotted, then a straight line is obtained for $\theta = 1$, a convex curve for $\theta < 1$, and a concave curve for $\theta > 1$ (Fig. 2). However, for most values of the parameter n, except for those close to the extremum, this dependence is linear and can be used — mainly in the region of the values of $n \ll n_e$ — in finding the correct direction and position of the tangent in the point $n(t = 0)$.

The slope of the straight line led through both points found with the aid of the conjugated pairs (actually, this is a tangent of the $t(1 - n) - \ln n$ curve in its left limiting point) is equal to $\theta/z_1 k_1[\text{Red}_1(t = 0)]$ and it allows us after the calculation of θ (on the basis of Eq. (*4g*) and experimentally found values of n_e and n_2) to determine the rate constant k_1.

Eq. (*4g*) can easily be solved graphically as the intersection of the horizontal $z = (1 - n_e)/n_e$ with the curve $z = (1 - n_2^\theta)/\theta n_2^\theta$ or by using the recurrent formula

$$\theta_{k+1} = \ln\{n_e/[n_e + \theta_k(1 - n_e)]\}/\ln n_2 \tag{4h}$$

with the starting approximation $\theta_0 = 1$.

For the determination of the rate constant, the point in which the slope of the tangent, $d\tau(1 - n)/d \ln n$, is equal to -1 is important. From this condition and Eq. (*4a*) we obtain an equation for the abscissa of the mentioned point

$$\theta + 1 = \frac{D}{\beta} n^\theta \frac{2n - 1}{(1 - n)^2} \tag{4i}$$

which together with Eq. (*4f*) gives

$$(p - x)^2 = wx^\theta(2x - p), \tag{4j}$$

where $x = n/n_e$, $p = 1/n_e$, and $w = (p - 1)^2 \theta/(\theta + 1)$. This transcendental equation for x can be solved by using the following rapidly converging recurrent formula

$$x_{k+1} = p + wx^\theta - [xw_k^\theta(p + wx_k^\theta)]^{1/2} \tag{4k}$$

with $x_0 = 1$ as the initial approximation. The determination of the value of x brings the possibility of another determination of the rate constant, since the tangent to the $t(1 - n) - \ln n$ curve in the point $n = xn_e$ has a slope equal to $-1/k_1 z_1$ . . $[\text{Red}_1(t = 0)]$. Moreover, the ratio of the slope of the tangent in the point $n(t = 0)$ to that in the point xn_e gives the value of θ and enables us to check graphically the value of θ calculated from Eq. (*4h*).

Curves for $D < 0$

For $D < 0$, the denominator in Eq. (*1*) becomes equal to zero if

$$D/\beta = (n_\infty - 1)/n_\infty^\theta . \tag{5a}$$

The $t(1 - n) - \ln n$ curve approaches a vertical asymptote with the abscissa $\ln n_\infty$ and is placed above the tangent led through the left limiting point and given by Eq. (*4c*) (Fig. 3). It is readily seen that the abscissae of the $t(1 - n) - \ln n$ curve in the case $D < 0$ must be diminished by certain values if the abscissae of the tangent in the left limiting point have to be obtained. Therefore, we rewrite the right-hand side of Eq. (*3a*) in the form of a fraction, which with the aid of Eq. (*5a*) takes the form

$$y + \ln \beta - \ln n_\infty = \ln \frac{n_1^\theta(1 - n_1 + D)}{n_\infty^\theta(1 - n_1) - (1 - n_\infty)\, n_1^\theta} = \ln \left(\frac{n_1}{n_2}\right)^\theta . \qquad (5b)$$

Now, the definition equation for the conjugated pair of n_1 and n_2 takes the form

$$n_2^\theta = [n_\infty^\theta(1 - n_1) - n_1^\theta(1 - n_\infty)]/(1 - n_1 + D) . \qquad (5c)$$

The straight line corresponding to Eq. (*5b*) is in Fig. 3 drawn by a broken line.

Since in practice we have always $|D| \ll 1 - n$, the value of D in Eq. (*5c*) can be neglected. To find the value of n_2^θ, the value of θ must be introduced into Eq. (*5c*), and this can be found as follows. In the point where both conjugated values of n_1 and n_2 are the same and equal to $\tilde{n}$, we have

$$\tilde{n}^\theta = [n_\infty^\theta(1 - \tilde{n}) - \tilde{n}^\theta(1 - n_\infty)]/(1 - \tilde{n} + D) . \qquad (6a)$$

In the mentioned point, the slope (*4a*) takes the form (assuming $|D| \ll 1 - n$)

$$\frac{d\tau(1 - n)}{d \ln n} = 2\theta - [\theta(\tilde{n}^2 - 2\tilde{n} + n_\infty) + (\theta - 1)\, \tilde{n}(1 - n_\infty)]/(1 - \tilde{n})^2 , \qquad (6b)$$

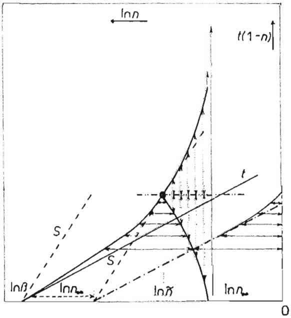

FIG. 3

Dependence of $t(1 - n)$ on $\ln n$ with a vertical asymptote; t tangent in the left limiting point, S its doubled slope as follows by combining equations *(4a)*, *(5a)*, and *(5c)*. The second term on the right-hand side represents only 3–4% of the value of 2θ, so that the slope in the point $\tilde{n}$ is practically equal to 2θ, *i.e.*, twice as large as in the left limiting point. When we have thus found the value of $\tilde{n}$, then from Eq. *(6a)* we obtain the value of θ as

$$\theta = \ln\left[(2 - \tilde{n} - n_{\infty})/(1 - \tilde{n})\right]/\ln\left(n_{\infty}/\tilde{n}\right). \qquad (6c)$$

At this point, we can draw the straight line $\bar{y} \sim \ln(n_1/n_2)$, from whose slope, which is equal to the tangent in the left limiting point (*i.e.*, $\theta/z_1k_1[\mathrm{Red}_1(t = 0)]$), we can calculate the rate constant k_1 using the known value of θ. The sign of the expression $\tilde{n}^2 - 2\tilde{n} + n_{\infty}$ is an additional characteristic of the ideal or nonideal behaviour of the electrode. Eq. *(6a)* can be rearranged to the form

$$v \equiv \tilde{n}^2 - 2\tilde{n} + n_{\infty} = n_{\infty}(\tilde{n} - 1)\left[(n_{\infty}/\tilde{n})^{\theta - 1} - 1\right], \qquad (6d)$$

so that $v = 0$ for $\theta = 1$, $v > 0$ for $\theta > 1$, and $v < 0$ for $\theta > 1$.

Note: If the electrode behaves ideally ($\theta = 1$), it is not necessary to calculate the conjugated values of n_2 from Eq. *(5c)*, since they can be determined graphically: the portion of the $t(1 - n) - \ln n$ curve above the point with the abscissa $\ln \tilde{n}$ is turned by 180° (Fig. 3) to form a curve with an extremum. This can be linearized with the aid of the conjugated pair $\ln(n_1/n_2)$ to obtain $z_1k_1[\mathrm{Red}_1(t = 0)]\,\bar{y} + \ln.$ $.(\beta/n_{\infty}) = \ln(n_1/n_2)$ with a slope $1/z_1k_1[\mathrm{Red}_1(t = 0)]$.

This follows from the fact that after turning, the right portion of the curve has the ordinate $\bar{\bar{y}}(n_2) = 2\bar{y}(\tilde{n}) - \bar{y}(n_2)$, whereas the left one has the ordinate $\bar{y}(n_1)$, and on the horizontals $\bar{y}(n_2)$ must be equal to $y(n_1)$. By expressing $\bar{y}(n_1)$, $\bar{y}(n_2)$, and $\bar{y}(\tilde{n})$ from Eq. *(1)* for $\theta = 1$, using the approximation $|D| \ll 1 - n$, Eq. *(5a)* and the definition of n *(6a)*, we obtain a relation between n_1 and n_2, which is identical with the definition of the conjugated pair *(5c)*.

Note: This graphical method, strictly valid for $\theta = 1$, can be used even for $\theta \neq 1$, since the conjugated pairs lie in this case on straight lines with a slope different from zero but small; moreover, the inclined branch of the curve is very steep. The obtained linear dependence has a slope equal to $\theta/z_1k_1[\mathrm{Red}_1(t = 0)]$.

Curves for $\beta = 0$

The $t(1 - n) - \ln n$ curves of this type are distinguished by the fact that they form only a descending arc. For $\beta = 0$, Eq. *(1)* simplifies to the form

$$\tau(1 - n) = \ln(1 - n + D) - \ln D \doteq \ln(1 - n) - \ln D, \qquad (7)$$

so that a linear relation exists between $t(1 - n)$ and $\ln(1 - n)$ with a slope equal to $1/z_1k_1[\mathrm{Red}(t = 0)]$, from which the rate constant k_1 can be determined.

Practical Method for Determining the Rate Constant

Based on the above theory, it is possible to proceed as follows. From the measured potential–time dependences with the parameter n, the dependences of $t(1 - n)$

on ln n for different preset potential values, E, are constructed. If it is not known whether the electrode behaves ideally (the case of solid electrodes), it is necessary to exclude linear dependences of $t(1 - n)$ on ln n (since their slope involves the value of θ, which in this case cannot be determined) and to use $t(1 - n)$ – ln n dependences obtained for other values of E = const.

If a descending arc is obtained, it is linearized in the cordinates $t(1 - n)$ – ln n with a slope equal to $1/z_1k_1[\mathrm{Red}_1(t = 0)]$.

In the case of $t(1 - n)$ – ln n dependences with a vertical asymptote, we find first the point ln $\tilde{n}$, in which the slope of the tangent is twice as large as that in the left limiting point. The branch of the curve above the point with abscissa ln $\tilde{n}$ is turned and the differences of the abscissae of the intersections of both branches with the horizontals $\bar{y} = t(1 - n)$ = const. are plotted against $\bar{y}$. The linear region of this dependence defines the slope of a straight line passing through the point with coordinates $n = 1$, $\bar{y} = t(1 - \tilde{n})$, *i.e.*, $\theta/z_1k_1[\mathrm{Red}_1(t = 0)]$, whence the constant k_1 can be calculated. The parameter θ follows from Eq. (*6c*) and the experimental values of $\tilde{n}$ and n_∞; its correctness can be checked by evaluating the right-hand side of Eq. (*3a*) for various values of n and plotting against $t(1 - n)$, whereby a straight line should be obtained. Incorrect determination of n_∞ leads to a curvature in the region of n values close to n_∞, incorrect determination of $\tilde{n}$ leads to deformation in the region of n values close to $\tilde{n}$.

In the case of the $t(1 - n)$ – ln n dependence with a maximum, the sum of the abscissae of its intersections with the horizontals $t(1 - n) = \bar{y}$ = const. is plotted against $\bar{y}$. If the resulting dependence is linear, then $\theta = 1$ and from its slope, $1/z_1k_1[\mathrm{Red}_1(t = 0)]$, the value of k_1 is calculated. Deviations from a linear dependence apparent mainly in the region of the maximum indicate that $\theta \neq 1$, nevertheless the initial portion of the curve thus obtained is linear and serves to construct the tangent in the left limiting point. The intersection of this tangent with that in the maximum point gives the value of n_2 conjugated to n_c, from Eq. (*4g*) the value of θ is calculated, and the constant k_1 is found from the slope of the tangent in the left limiting point, $\theta/z_1k_1[\mathrm{Red}_1(t = 0)]$. Alternatively, the value of x can be calculated from Eq. (*4k*) to give the coordinate xn_c of the point in which the tangent has a slope equal to $-1/z_1k_1[\mathrm{Red}_1(t = 0)]$, then the value of k_1 can be found, and the ratio of the slopes in the left limiting and in the point $n = xn_c$ gives the value of θ for the purpose of checking. Another check of the correctness of the found value of θ is the calculation of the right-hand side of Eq. (*3a*) (the right-hand side of Eq. (*4j*) multiplied with $n(t = 0)^\theta$ is substituted for D) for various values of n and plotting against $t(1 - n)$; the ascending and descending branches should lie on the same straight line with a slope equal to $1/k_1z_1[\mathrm{Red}_1(t = 0)]$, whereas in the case of an error in the value of θ a peak is formed.To facilitate these calculations, a program was elaborated for the TI 59 calculator, which is available by the authors.

The most critical step in the above calculations is the determination of θ from Eq. (*6c*) or (*4g*), since a change in the value of $n_2 - n_e$ or $n_\infty - \tilde{n}$ by 0·01 brings about a change in the value of θ by 0·2 on the average. Therefore, in the case of curves with an extremum it is recommended to check the value of θ by the ratio of the slopes of both the mentioned tangents. Since for experimental reasons the value of n cannot be determined more accurately than to within $\pm 0{\cdot}01$, the values of θ are subject to a relative error of $\pm 10\%$.

For illustration, Eq. (*1*) was solved for various values of the parameters to obtain the unknowns θ and k_1 (Table I). Their values were, for comparison, calculated also by the optimization method of an elastic polyhedron[3].*

It follows from the results that our graphical-numerical method for the determination of the rate constant is relatively rapid and works with a maximum relative error of 10%, which is satisfactory in practical cases. Otherwise, the values thus found can be used as starting values in the optimization procedure leading to more accurate values of D, β, θ, and k_1 in Eq. (*1*).

From the point of view of the use in reaction kinetics, the following conclusion can be arrived at: Although the treatment of experimental data based on the use of nonequilibrium potentials for following the reaction course is more complicated than in the case of quantities depending linearly on the composition of the reaction mixture (*e.g.*, absorbancy), on the other hand, there is an advantage in universality, possibility of miniaturization in combining the indicator and reference electrodes in the form of a microsensor, and finally the possibility of remote detection. This is important in cases where the reaction space is very small or difficultly accessible to other measuring devices.

TABLE I

Comparison of preselected and found parameter values

Given				Found graph.-numer.		Optimization				No. of iter.
β	D	θ	k_1	k_1	θ	β	D	θ	k_1	
0·0075	0·03	2	100	91	1·9	0·0079	0·03	1·975	98·7	200
0·1	0·035	0·5	100	109	0·56	0·094	0·034	0·514	102·5	123
0·05	0·15	1	100	93	0·95	0·050	0·154	1·000	98·5	83
0·01	−0·001	2	100	98	1·97	0·01	−0·001	1·984	99·3	490

* We have also used 5 other derivative-free and derivative methods but only the referred one was succesfull in all cases.

REFERENCES

1. Tockstein A., Skopal F.: This Journal *39*, 3016 (1974).
2. Tockstein A., Skopal F.: This Journal *39*, 1518 (1974).
3. Himmelblau D. M.: *Process Analysis by Statistical Methods.* Wiley, New York 1969.

Translated by K. Micka.