ANALYSIS OF ASYMMETRIC SIGMOID KINETIC CURVES OF AUTOCATALYTIC REACTIONS

Tomáš FAZEKAŠ, Arpád NAGY and Ľudovít TREINDL*

Department of Physical Chemistry,
Comenius University, 842 15 Bratislava, The Slovak Republic

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Dedicated to Professor Vladislav Holba on the occasion of his 60th birthday.

A new procedure for the analysis of sigmoid autocatalytic curves was developed based on the simulated annealing method. The procedure is particularly well suited to the treatment of asymmetric sigmoid shapes. The method was applied to the autocatalytic oxidation of citric acid with potassium permanganate.

Autocatalytic reactions have been attracting interest in connection with investigation into nonlinear chemical processes. The black-box model suits well if not all elementary steps constituting the autocatalytic reaction in question are known; within that model, only the input and output concentrations are known whereas the detailed mechanism is hidden in the black-box. In some cases, simple properties of autocatalytic reactions such as the inflection point and the induction period can be modelled by means of low degree polynomial functions or suitable spline curves. However, the fact that such procedures provide no quantity that can be interpreted as the rate constant is a disadvantage.

THEORETICAL

Rate constants of autocatalytic reactions usually do not lend themselves to calculation by the least squares method. The rate equation of autocatalytic reactions can be written as[1]

$$-\mathrm{d}x/\mathrm{d}t \quad = \quad k\, y^n\, g(x)\,, \qquad (1)$$

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* The author to whom correspondence should be addressed.

where k is the reaction rate constant, y is the actual concentration of the autocatalytically active component Y, function $g(x)$ expresses the effect of reactant X on the reaction rate, and n is the partial reaction order.

Integration of Eq. (*1*) leads to rather complex expressions that may be difficult to linearize or from which the concentration of substance X cannot be expressed explicitly. The presence of the autocatalytically active component Y at the beginning (in time $t = 0$) poses a serious problem. Equations (*2*) and (*4*) a priori presume the occurrence of substance Y whereas in the remaining pathways the first quantities of substance Y only form in a parallel reaction step.

Assume that the autocatalytic species emerges from a reaction of substrate X and product Y according to Eq. (*A*) and no side reactions take place.

$$X + Y \longrightarrow 2Y + P \qquad (A)$$

The occurrence of product Y at the beginning of the reaction at a concentration $y_0 > 0$ is a prerequisite for the reaction to set in. Assume that the mass balance $y = x_0 + y_0 - x$ is obeyed (x_0 is the starting concentration od reactant X and x and y are the actual concentrations); then the rate equation

$$-\mathrm{d}x/\mathrm{d}t = k\,x\,(x_0 + y_0 - x) \qquad (2)$$

applies. Integration and rearrangement lead to a dependence from which the rate constant can also be calculated by the linear method of least squares. Indeed, plotting the right-hand side of Eq. (*2*) as a function of time we obtain

$$k\,t + \frac{1}{x_0 + y_0}\ \ln\,(y_0/x_0) = \frac{1}{x_0 + y_0}\ \ln\frac{x_0 + y_0 - x}{x} \qquad (3)$$

which is a linear dependence whose slope gives the rate constant.

The sigmoid curve described by Eq. (*2*) is symmetric with respect to the inflection point in the reactant concentration vs time coordinates. The inflection point occurs at one-half of the substance conversion (we have $x_0 >> y_0$). Actually, this is seldom true of autocatalytic curves, the inflection point being shifted to higher or lower substance conversion degrees. The course of an autocatalytic reaction with a shifted inflection point, corresponding to reaction (*A*), can be described by the equation[1]

$$-\mathrm{d}x/\mathrm{d}t = k\,x\,(x_0 + y_0 - x)\,/\,(x + q)\,, \qquad (4)$$

where parameter q is a function of the degree of substance conversion at the inflection time,

$$q = \frac{x_{\mathrm{it}}^2}{x_0 + y_0 - 2\,x_{\mathrm{it}}} \qquad (5)$$

(symbol x_{it} denotes the concentration of reactant X in the inflection point). The rate constant is calculated from the linear equation

$$kt + \frac{q}{x_0 + y_0} \ln \frac{y_0}{x_0} = -\frac{q}{x_0 + y_0} \ln \frac{x}{x_0 + y_0 - x} + \ln \frac{x_0 + y_0 - x}{y_0} \qquad (6)$$

by the least squares method.

The two types of autocatalysis described by Eqs (*2*) and (*4*), respectively, are rather rare in practice. The starting amount of the autocatalytically active substance is present in these systems as an "impurity", i.e. as a product of spontaneous decomposition of the reactant during storage, preparation of solutions, etc. The results of calculations are very sensitive to the starting concentrations x_0 and y_0.

Frequently, occurrence of the autocatalytic species at the very beginning of the reaction is ruled out by the reaction conditions. The presence of such species can be affected, for instance, by complexing side equilibria or by the instability of the species in the given medium. In such cases, models are used where, in addition to the autocatalytic reaction, there is involved a simple parallel reaction step during which the starting quantity of the autocatalytic species is formed

$$\begin{aligned} X + Y &\longrightarrow 2Y + P \\ X &\longrightarrow Y + Q \end{aligned} \qquad (B)$$

The equation

$$-\mathrm{d}x/\mathrm{d}t = k_n x + k_a x (x_0 - x) \qquad (7)$$

has been applied by the authors[2] to the evaluation of the oxidation kinetics of various organic substrates with potassium permanganate[3 - 11]; in this equation, k_n is the rate constant of the noncatalyzed reaction and k_a characterizes the autocatalytic reaction. The authors proposed two calculation methods, viz. a differential method and an integral method. The latter is an iterative procedure, where the rate constants are calculated by the linear least squares method based on the equation

$$\ln \frac{k_n + k_a x_0 - k_a x}{x} = \ln \frac{k_n}{x_0} + (k_n + k_a x_0)\, t\,. \qquad (8)$$

The starting rate constant estimates are iteratively refined until a preselected convergence criterion is satisfied, e.g. $W_a(k_a^i - k_a^{i+1})^2 + W_n(k_n^i - k_n^{i+1})^2 < \mathrm{TOL}$, where *i* refers to the iteration cycle, *W*'s are calculation precision weights and TOL is tolerance. Schwartz[12] used the explicit expression for the concentration

$$x = \frac{b}{k_a x + k_n e^{bt}}, \quad \text{where } b = k_n + k_a x_0 \tag{9}$$

and optimized the rate constants by the simplex method. He was able, by additional optimization of the starting concentration x_0 within the region of $x_0 \pm 0.001\, x_0$ to reduce the standard deviation with respect to the initial value and to eliminate oscillation of experimental points about the straight line obtained.

The reaction scheme (*B*) is a case for which the concentration coordinate of the inflection point lies at half height of the sigmoid curve (we have $x_0 >> y_0$). If Eq. (*A*) is augmented with a noncatalytic parallel first order reaction, the rate equation becomes

$$-\mathrm{d}x/\mathrm{d}t = k_n x + k_a x\,(x_0 - x)/(x + q) \tag{10}$$

and its solution is unsymmetrical with respect to the inflection point in coordinates *t* and *x*. By integrating Eq. (*10*) and rearranging we obtain a linear relationship between the left-hand and right-hand sides,

$$q \ln(x) + \frac{k_a x_0 + q\, k_a}{k_n - k_a} \ln(k_n x - k_a x + k_n q + k_a x_0) = -(k_n q + k_a x_0)\, t + C, \tag{11}$$

where *C* is the integration constant defined by the relation

$$C = q \ln(x_0) + \frac{k_a x_0 + q\, k_a}{k_n - k_a} \ln(k_n x_0 + k_n q). \tag{12}$$

Concentration of reactant X cannot be explicitly expressed from Eq. (*11*). Therefore we used the inverse function in the form of $t = f(x)$ which expresses time as a function of concentration of substance X, and optimized this function by the simulated annealing method[13]. We minimized the expression $\sum_{i=1}^{n} | t^i_{\mathrm{obs}} - t^i_{\mathrm{calc}} | /n$, where the subscripts obs and calc refer to the observed and calculated time values.

This optimization procedure was developed based on a physical interpretation of the process of crystallization of a molten solid. If the state which is most favourable from the energy aspect, i.e. the single crystal state, is to be achieved, the crystallization has to be accomplished slowly enough for the thermodynamic equilibrium to establish at each cooling temperature. The simulation of thermal evolution of the system proceeds via minor defects (a sequence of configurations with different geometries) which are generated at random from the previous states by displacing a randomly selected particle according to certain rules. If the total energy of the disturbed system is lower than the energy of the preceding configuration, new coordinates of the selected particle are adopted; otherwise, the probability of adopting the new state depends on the $\exp(-\delta E/kT)$ value, where δE is the total energy change, k is the Boltzmann constant and T is thermodynamic temperature. After a sufficiently high number of iterations, the system attains its thermodynamic equilibrium at the given temperature. This procedure is repeated until the termination conditions, i.e. freezing of the system, is reached.

The noncatalyzed parallel reaction can be second order with respect to reactant X. This is represented by the scheme

$$\begin{array}{rcl} \mathrm{X + Y} & \longrightarrow & \mathrm{2\,Y + P} \\ \mathrm{2\,X} & \longrightarrow & \mathrm{Y + Q} \end{array} \tag{C}$$

for which the rate constant is obtained in the form

$$-\mathrm{d}x/\mathrm{d}t = k_n x^2 + k_a x(x_0 - x)/(x + q)\,. \tag{13}$$

Integration within the limits of 0 to t gives

$$t + C = \frac{q}{2z}\ln\frac{x^2}{r} + \frac{2z - qw}{z}\frac{1}{\sqrt{r}}\,\mathrm{arctg}\frac{2vx + w}{\sqrt{r}}\,, \tag{14}$$

where $r = |vx^2 + wx + z|$. Parameters v, w and z are defined as follows: $v = k_n$, $w = k_n q - k_a$, $z = k_a x_0$. The integration constant C is expressed as

$$C = \frac{q}{2z}\ln\frac{x_0^2}{r_0} + \frac{2z - qw}{z}\frac{1}{\sqrt{r_0}}\,\mathrm{arctg}\frac{2vx_0 + w}{\sqrt{r_0}}\,, \tag{15}$$

where $r_0 = |vx_0^2 + wx_0 + z|$. By combining schemes ($B$) and ($C$) we obtain a reaction scheme which describes an autocatalytic system comprising the following three parallel steps.

$$\begin{array}{rcl} \mathrm{X + Y} & \longrightarrow & \mathrm{2\,Y + P} \\ \mathrm{2\,X} & \longrightarrow & \mathrm{Y + Q} \\ \mathrm{X} & \longrightarrow & \mathrm{Y + R} \end{array} \tag{D}$$

The corresponding rate equation is

$$-\mathrm{d}x/\mathrm{d}t = k_L x + k_Q x^2 + k_a x(x_0 - x)/(x + q)\,, \tag{16}$$

where k_L and k_Q are the rate constants of the first order and second order reactions, respectively. Integration gives again expression (*14*), where, however, parameters v, w, z have a different meaning, namely, $v = k_Q$, $w = k_L + k_Q q - k_a$, and $z = k_L q + k_a x_0$.

EXPERIMENTAL

The reaction of citric acid with potassium permanganate in a sulfuric acid solution was used to test the calculation procedure. The reaction conditions were as follows: $[KMnO_4]_0$ = 0.4 mmol dm^{-3}, $[C_6H_7O_8]_0$ = 300 mmol dm^{-3}, $[KMnO_4]_{it}$ = 0.119 mmol dm^{-3}, $[Mn^{2+}]_0$ = 0.005 mmol dm^{-3}, $[H_2SO_4]_0$ = 500 mmol dm^{-3}, temperature 25 °C.

The reaction was monitored by two independent methods, spectrophotometrically and polarographically. For the former, the wavelength was 525 nm, optical path length 1 cm. The reaction system was stirred with an electromagnetic stirrer and was thermostatted to within ±0.1 °C. Concentrations were calculated from absorbances by using Beer's law.

The polarographic measurements were performed in a thermostatted Kalousek's vessel. A rotating platinum electrode and a 1 M mercurous sulfate electrode served as the indicator and reference electrodes, respectively. The time dependence of the actual potassium permanganate concentration was calculated, by means of a calibration curve, from the time behaviour of the limiting polarographic current at an applied voltage of 0 V.

Calculations using concentrations which were obtained by the two kinds of measurement gave statistically identical results.

RESULTS AND DISCUSSION

Since the model reaction consisted in the autocatalytic oxidation of citric acid with potassium permanganate, we expected – based on refs[3 – 11] – that Eq. (*8*) would be applicable to the description of the time dependence of concentration of permanganate ions.

The integral method[2] was used. Convergence of the method for the reaction system in question was tested (Fig. 1), and identical final values were obtained from different starting estimates of the rate constants k_n and k_a. The target function converged rapidly. Five to twenty iterations had to be used, in dependence on the tolerance conditions. The resulting rate constants, viz. $k_n = 2.98 \cdot 10^{-5}\ s^{-1}$, $k_a = 22.06\ dm^3\ mol^{-1}\ s^{-1}$, were inserted in Eq. (*9*) for the calculation of the theoretical reaction course. Figure 2 demonstrates that the method is unsuitable for treating the reaction studied.

The time behaviour of the permanganate ion concentration exhibits an inflection point which is markedly shifted to lower concentrations, viz. to 0.119 mmol dm^{-3}. The solution of Eq. (*4*) possesses such a property as well. Therefore we inserted values from the time course of the reaction into the straight line Eq. (*6*). The numeric parameter to be entered was calculated from Eq. (*5*). The permanganate ion concentration in the inflection point was determined from the time course of the reaction. The starting concentration of the autocatalytically active component was entered into the calculations as an optimized parameter ($[Mn^{2+}]_0$ = 0.005 mmol dm^{-3}). The reaction rate constant was determined to be $k = 0.006\ s^{-1}$ and served to calculate the theoretical time behaviour of permanganate ion concentrations (Fig. 3). Of the methods used, the second was found to be better suited to the reaction examined. It is a shortcoming of that method, however, that the starting concentration of the autocatalytic species mostly cannot be determined and must be entered as an optimized parameter.

This shortcoming of the approach (*4*) was obviated by using scheme (*C*), where a parallel reaction is the source of the initial quantity of the catalytically active reactant.

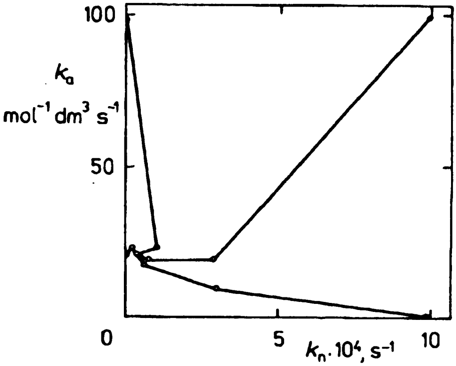

FIG. 1

Convergence of consecutive iterations in the calculation of the rate constants of the model reaction using different starting values

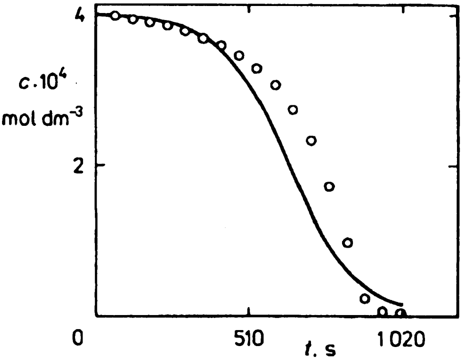

FIG. 2

Course of the model reaction: ○ observed values, —— calculated by means of Eq. (*9*)

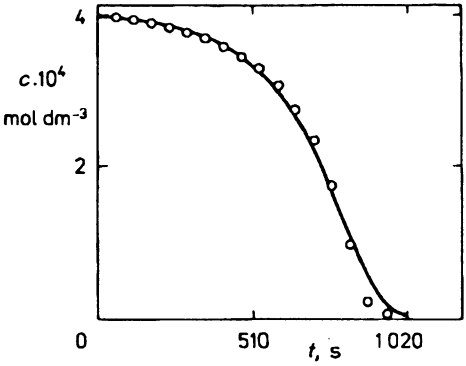

FIG. 3

Course of the model reaction: ○ observed values, —— calculated by means of the integral form of Eq. (*4*)

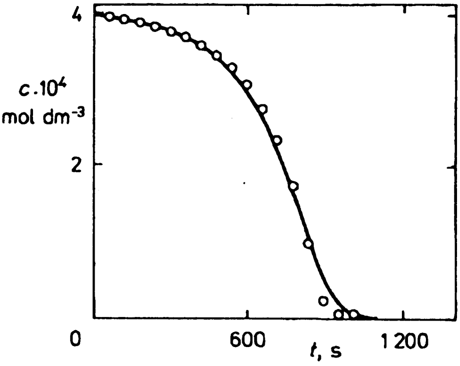

FIG. 4

Kinetic curve of reduction of permanganate ions with citric acid: ○ observed values, —— calculated by the simulated annealing method

The rate constants k_a and k_n were obtained by the simulated annealing method. The inverse function to the initial time behaviour of the permanganate ion concentration was employed in the calculation. A higher number of configurations (N_c = 32 530) had to be calculated to achieve a good convergence, the target function value decreased to 15.7 s. The optimized rate constants were k_a = 0.006178 s^{-1} and k_n = 0.18101 dm^3 mol^{-1} s^{-1}. The time dependences of the observed and calculated potassium permanganate concentrations are shown in Fig. 4.

The results of calculation via Eq. (*8*) suggest that the underlying mechanism of oxidation of citric acid with potassium permanganate differs from that of the substrates studied in refs[3] – [11]. The reaction is autocatalytic under the conditions applied, and the reaction system remains homogeneous throughout the entire course of the reaction. In contrast to the cases cited, Mn^{2+} ions are likely to be the autocatalytically active species[14].

A comparison of the calculated rate constants suggests that the autocatalytic step dominates the reaction. The rate of the parallel reaction step is so low that this step apparently only plays an important part when the autocatalytic reaction sets in, whereas it has virtually no effect on the further reaction course.

Computer processing of the kinetic curves of autocatalytic reactions can be of assistance in the prediction[15] of regions of kinetic bistabilities in flow conditions.

REFERENCES

1. Póta Gy., Bazsa Gy: J. Chem. Soc., Faraday Trans. 1 *84*, 215 (1988).
2. Mata-Perez F., Perez-Benito J. F.: J. Chem. Educ. *64*, 925 (1975).
3. Andres J., Garrido J. A., Perez-Benito F.: J. Chem. Soc., Perkin Trans. 2 *107*, (1988).
4. Perez-Benito F., Mata-Perez F., Brillas E.: Can. J. Chem. *65*, 2329 (1988).
5. Brillas E., Garrido J. A., Perez-Benito F.: Collect. Czech. Chem. Commun. *53*, 479 (1988).
6. Garrido J. A., Perez-Benito F., Rodriguez R. M., Brillas E.: J. Chem. Res. *1978*, 380.
7. Rodriguez R. M., Andres J., Brillas E., Garrido J. A., Perez-Benito J. F.: New. J. Chem. *12*, 143 (1988).
8. Andres J., Brillas E., Garrido J. A., Perez-Benito J. F.: Gazz. Chim. Ital. *118*, 203 (1988).
9. Mata-Perez F., Perez-Benito F.: Z. Phys. Chem. *267*, 120 (1986).
10. Mata-Perez F., Perez-Benito F.: Can. J. Chem. *65*, 2373 (1987).
11. Lee D. G., Perez-Benito F.: Can. J. Chem. *63*, 1275 (1985).
12. Schwartz L. M.: J. Chem. Educ. *66*, 677 (1989).
13. Černý V.: *Preprint Series in Theoretical Physics HU-TFT-84-51*. Research Institute for Theoretical Physics, University of Helsinki, Helsinki 1984.
14. Kalra H. L., Ghose S.: J. Pract. Chem. *30*, 6 (1965).
15. Fazekaš T., Nagy A., Treindl L.: Unpublished results.

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