

Mapping in Kinetic Time Series

W. P. Savel'yanov

Novomoskovsk Institute, Mendeleev University of Chemical Technology, Novomoskovsk, Tula oblast, Russia

Received July 28, 2003

Abstract—It is suggested to treat kinetic data as time series. Mapping formulas in the form of a generalized linear functional equation are derived for the most typical kinetic systems. These formulas are applicable to the analysis of experimental kinetic data.

Much progress has been made in the development of kinetic data analysis techniques aimed at the identification of probable kinetic models and at the estimation of model parameters such as rate constants and partial reaction orders (see, e.g., [1–4]). Standard data analysis methods include construction of linear anamorphoses for kinetic curves, analysis of (initial) reaction rates, and numerical integration of probable rate equations with minimization of the sum of squared deviations of calculated data from observed data. This report deals with the application of mapping to the analysis of kinetic data for a batch reactor (a closed system).

The applicability of this technique follows directly from the fact that kinetic data are time series of observed values (key component concentrations or quantities proportional to them). In the last few decades, processing of time series has attracted much attention as a tool for investigation of complicated dynamic systems [5]. We will consider only series of kinetic measurements taken at regular time intervals.

In most cases, processing kinetic data reduces to constructing a probable kinetic model followed by checking this model against experimental data. A kinetic model itself is nothing but a theoretically substantiated ordinary differential equation relating the reaction rate to the concentrations of key components. It is well known that any ordinary differential equation allows construction of a mapping equation relating the $(i + 1)$ th term of the series of observed values (measured while giving equal increments to the independent variable) to some function of a sequence of the preceding terms [4]. In the simplest case, a term of the series is a function of its antecedent:

$$x_{i+1} = f(x_i) \quad i = 0, 1, 2, \dots \quad (1)$$

The method of deriving such mapping formulas for differential equations integrable in quadratures is simple and can be illustrated by applying it to a (pseudo)first-order reaction (Table 1, row 1). For mea-

Table 1. Mapping formulas for kinetically simple reactions

Reaction	Rate equation	Mapping formula	Notes
$A \xrightarrow{k} B$	$-\frac{dc}{d\tau} = kc$	$c_{n+1} = c_n R$	$R = \exp(-k\Delta\tau)$
$A \xrightarrow{k} B$	$-\frac{dc}{d\tau} = kc^m$	$\frac{1}{c_{i+1}^{m-1}} = \frac{1}{c_i^{m-1}} + R$	$R = k(m-1)\Delta\tau = \text{const}$ $m \neq 1$
$A + B \xrightarrow{k} C$	$-\frac{dc_A}{d\tau} = kc_A c_B$	$\frac{1 - x_{i+1}}{\beta - x_{i+1}} = \frac{1 - x_i}{\beta - x_i} R$	$R = \exp(kc_{A,0}(\beta - 1)\Delta\tau) = \text{const}$ $x = \frac{c_{A,0} - c_A}{c_{A,0}} \quad \beta = \frac{c_{B,0}}{c_{A,0}}$
$A + B \xrightarrow{\frac{1}{2}} C + D$	$-\frac{dc_A}{d\tau} = k_1 c_A c_B - k_2 c_C c_D$	$\frac{x_{i+1} - x_1}{x_{i+1} - x_2} = \frac{x_i - x_1}{x_i - x_2} R$	$R = \exp(-(x_1 - x_2)k_1\Delta\tau) = \text{const}$ $c_{C,0} = c_{D,0} = 0$ $x = \frac{c_{A,0} - c_A}{c_{A,0}} \quad \beta = \frac{c_{B,0}}{c_{A,0}} \quad K = \frac{k_1}{k_2}$ $x_{1,2} - \text{roots of the equation}$ $c_{A,0}(1 - x)(\beta - x) - K^{-1}x^2 = 0$

Table 2. Mapping formulas for complicated kinetic systems

Reaction	Rate equation	Mapping formula	Notes
$M + K \xrightleftharpoons{K} MK \xrightarrow{+M} P$	$-\frac{dM}{d\tau} = \frac{kM^2 c_{K,0}}{1 + KM}$	$\frac{1}{M_{i+1}} + K \ln M_{i+1} = \frac{1}{M_i} + K \ln M_i + R$	$R = -k\Delta\tau = \text{const}$ $M = C_M$
$M + K \xrightleftharpoons[-1]{1} MK \xrightarrow{k_2} P$	$-\frac{dM}{d\tau} = \frac{kM c_{K,0}}{1 + KM}$	$M_{i+1} + K \ln M_{i+1} = M_i + K \ln M_i + R$	$K = \frac{k_{-1} + k_2}{k_1}$ $R = -k_2 c_{K,0} \Delta\tau = \text{const}$
$A \xrightarrow{1} B \xrightarrow{2} C$	$-\frac{dA}{d\tau} = k_1 A$ $+\frac{dB}{d\tau} = k_1 A - k_2 B$	$A_{i+1} = A_i R$ $\frac{B_{i+1}}{A_{i+1}} = (\kappa - 1) \frac{B_i}{A_i} + \frac{1 - e_2}{\kappa - 1}$	$e_1 = \exp(-k_1 \Delta\tau)$ $e_2 = \exp(-\kappa \Delta\tau)$ $R = e_1 \quad \kappa = \frac{k_2}{k_1}$
$I \xrightarrow{0} 2I^*$ $I + M \xrightarrow{i} IM$ $IM^* + M \xrightarrow{p} IM_2^* \dots$ $IM_p^* + IM_q^* \xrightarrow{t} P$	$-\frac{dM}{d\tau} = kMI^{0.5}$	$\frac{2}{\alpha_K} + \ln \frac{M_{i+1}}{M_0} = \left(\frac{2}{\alpha_K} + \ln \frac{M_i}{M_0} \right) R$	$R = \exp\left(-\frac{k_0 \Delta\tau}{2}\right)$ $\alpha_K = \frac{k_0}{k_{\text{eff}} I_0^{0.5}} \quad k = k_{\text{eff}} = k_p \left(\frac{k_0}{k_i}\right)^{0.5}$

measurements separated by regular time intervals $\Delta\tau$, the integral equation for the time point $n\Delta\tau$ will appear as

$$c_n = c_0 \exp(-kn\Delta\tau) \quad n = 0, 1, 2, 3, \dots \quad (2)$$

Hence, we readily obtain the mapping formula

$$\begin{aligned} c_{n+1} &= c_0 \exp(-k(n+1)\Delta\tau) \\ &= c_0 \exp(-kn\Delta\tau) \exp(-k\Delta\tau) = c_n \exp(-k\Delta\tau), \end{aligned} \quad (3)$$

or

$$c_{n+1} = c_n \text{const}, \quad (4)$$

since $k\Delta\tau$ is constant.

It follows from Eq. (4) that this mapping is linear, and the slope of the correlation line defines a unique reaction rate constant:

$$k = -\frac{\ln \text{const}}{\Delta\tau}. \quad (5)$$

This type of mapping formula can readily be obtained for all kinetically simple (Table 1) and some complex systems. In Table 2, we present mapping formulas for catalytic ionic polymerization, Michaelis–Menten enzyme kinetics, free-radical polymerization (all in the steady-state approximation for active intermediates), and a sequence of consecutive reactions. Although the mapping for the consecutive reactions is two-dimensional, it is still possible to find an adequate mapping function.

Clearly, all these mappings allow generalization in the following form:

$$f(x_{n+1}) = \begin{cases} f(x_n)g(k, \Delta\tau) = f(x_n)\text{const} \\ f(x_n) + g(k, \Delta\tau) = f(x_n) + \text{const}, \end{cases} \quad (6)$$

where $f(x)$ is some function of the measured variables and $g(k, \Delta\tau)$ is a function of the parameters and of the measurement step size, both functions being independent of step number. The latter function is invariant for a given array of observations since its value is constant throughout this array. Invariants can be used in rough discrimination of kinetic models (see the invariable rate constant method [2]). Indeed, Eq. (6) implies the following simple relationships:

$$\begin{aligned} f(x_{i+1}) - f(x_i) &= (f(x_i) - f(x_{i-1}))\text{const}, \\ f(x_{i+1}) - f(x_i) &= (f(x_i) - f(x_{i-1})), \end{aligned} \quad (7)$$

which allow one to find $f(x)$ ensuring constancy of the invariant.

Thus, in these kinetic time series, any term is equal to the preceding term either multiplied by an invariant or added to an invariant. These relationships are true even for the ratio of the concentration of the first product to the concentration of the original substance in a system of consecutive reactions. It is also significant that these mappings are functional; that is, in the space of observations (which is one-dimensional in the case considered), there is a function whose values for a given and the subsequent measurement are interrelated. By contrast, point mappings like Eq. (1) directly interrelate these measurements. We demonstrate in Tables 1 and 2 that relationships like Eq. (1) in explicit form cannot be derived from mapping formulas even for simple kinetic systems because of the transcendence of the mapping functions. Therefore, functional relationships like Eq. (6) are more general than identity (1) and it can be assumed that they must be more frequent in time series.

It can readily be seen that the mapping formulas listed in Tables 1 and 2 allow experimental data to be processed in unconventional ways. For example, the following linear relationship must be valid for free-radical polymerization:

$$\ln \frac{M_{n+1}}{M_0} = \frac{2}{\alpha_K} (R-1) + R \ln \frac{M_n}{M_0}. \quad (8)$$

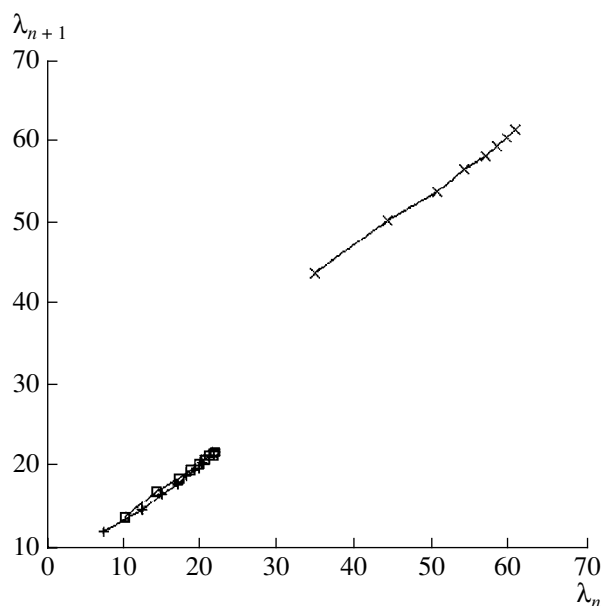
This equation allows the initiation (initiator decomposition) rate constant and the effective reaction rate constant to be estimated from the slope angle and ordinate intercept, respectively (see the expressions for R and the polymerization constant α_K [6] in Table 2).

Some interesting specific features of the mapping method can be illustrated by processing electric conductivity data for reactions between phosphorus oxychloride and alcohols, which were studied by the stopped-flow method using a loop oscillograph [7, 8]. In the original study, the rate constant of this reaction was derived from the integral kinetic equation

$$\ln \frac{\lambda_\infty - \lambda}{\lambda_\infty - \lambda_0} = -k\tau, \quad (9)$$

where λ is the electric conductivity of the reaction mixture and the subscripts ∞ and 0 mean measurements at an infinite time (when the reaction is complete) and at the instant the reaction is started, respectively. Direct proportionality between the electric conductivity of the reaction mixture and the hydrogen chloride concentration was established in an earlier study [6].

The figure plots data processed using the mapping formula (2) for three runs at 24.8°C. (The marked difference between the mappings is due to the fact that electric conductivities are used instead of concentrations.) Least-squares regression leads to the rate constant array 4.214, 4.300, 4.135 s⁻¹ with a one-run variance of $\sim 2 \times 10^{-5}$. Classical processing of the same data leads to the array 4.500, 4.232, 4.044 s⁻¹ with a variance of about 3×10^{-4} . Clearly, as determined from the results of three runs, the reproducibility variance of the rate constant is smaller in the former case than in the



Intensity of an oscillographic signal versus the intensity of the preceding signal for three ethanol-phosphorus oxychloride reaction runs at 24.8°C [7].

latter. This is undoubtedly due to the fact that taking the logarithm of the decreasing difference between oscillographic signal intensities adds to the error. Therefore, in this case, the mapping method is somewhat superior to the conventional integral method from the standpoint of data reliability.

This inference is likely to be true in other cases as well, as is suggested by the results of data processing for an irreversible mixed-second-order reaction (Table 3). Error analysis was carried out for the following model: initial concentration of the key substance (A), 2 mol/l; excess coefficient of substance B, $\beta = 1.5$; rate constant, $k = 2 \times 10^{-3}$ (mol/l)⁻¹ s⁻¹; time step size, 180 s; and ultimate conversion, 0.987. The random error was simulated by superimposing, on the current

Table 3. Results of data processing for a second-order irreversible reaction

Processing method	$k \times 10^3, \text{l mol}^{-1} \text{s}^{-1}$			Correlation factors at $s_A^2 = 1 \times 10^{-2}$
	$s_A^2 = 1 \times 10^{-4}$	$s_A^2 = 1 \times 10^{-3}$	$s_A^2 = 1 \times 10^{-2}$	
Mapping	2.000	1.999	2.001	0.996
	2.000	1.997	2.004	0.995
	2.000	1.998	2.002	0.997
Classical method	2.002	1.991	1.907	0.978
	2.000	2.011	1.998	0.996
	1.998	1.983	1.996	0.975
Middle-invariant method	2.003	1.983	1.785	1.000
	2.003	1.982	1.783	1.000
	1.999	1.972	1.444	1.000

Note: s_A^2 is the variance of the concentration of the key reactant A.

concentration of A derived from the kinetic equation, a normally distributed random variable with a zero expectation and three different values of variance, specifically, 1×10^{-4} , 1×10^{-3} , and 1×10^{-2} . Thus, we assumed that the absolute error in the concentration of the key component is constant (as is usually the case in kinetic measurements). It is clear from the data presented in Table 3 that the mapping method affords more reliable results than the classical integral method not only for small and intermediate variances but also for an unreasonably large variance of 1×10^{-2} . As mentioned above, this is due to the fact that taking the logarithm of small differences increases the error. Since logarithms are frequent in integral kinetic equations, arising from the integration of fractional rational functions typical of kinetics, the inference as to the reliability of the mapping method is quite general. Note that even the middle-invariant (invariable rate constant [2]) method is reliable only for fairly accurate measurements.

Another specific feature of the mapping method is that it is unnecessary to know the initial conditions (the initial concentration of the key reactant), which cannot be reliably determined in some cases, e.g., for fast reactions. This feature is common to most of the kinetic systems considered here (Tables 1, 2). This circumstance makes it easier to deduce possible kinetic models from experimental data.

Thus, mapping formulas can be obtained for typical simple kinetic systems and can be used to derive parameters of kinetic equations (partial orders of reaction, rate constants, etc.) from experimental data.

In conclusion, note the following significant points. First, rather simple mapping formulas can be obtained only for differential kinetic equations integrable

through separation of variables. In more general cases, including fractional-order reactions (Table 1, row 2), the constant R appears to depend on the formal measurement number. Nevertheless, this is not a serious obstacle that can limit the applicability of the mapping method. The second noteworthy point is that the main applicability condition for the above mapping formulas is the equality of time intervals between measurements, $\Delta\tau$. Therefore, the use of these formulas is limited to the case of continuous recording of key reactant concentrations (or proportional quantities) and to measurements taken at regular time intervals.

REFERENCES

1. Emmanuel, I.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Vysshaya Shkola, 1974.
2. Jungers, J.C. and Sajus, L., *L'analyse cinetique de la transformation chimique*, Paris: Technip, 1967–1968.
3. Lebedev, N.N., Manakov, M.N., and Shvets, V.F., *Teoriya tekhnologicheskikh protsessov osnovnogo organicheskogo i neftekhimicheskogo sinteza* (Theory of Basic Organic and Petrochemical Synthesis Processes), Moscow: Khimiya, 1984.
4. Schmid, R. and Sapunov, V.N., *Non-formal Kinetics: In Search for Chemical Reaction Pathways*, Weinheim: Chemie, 1982.
5. Malinetskii, G.G. and Potapov, A.B., *Sovremennye problemy nelineinoi dinamiki* (Current Problems of Nonlinear Dynamics), Moscow: URSS, 2000.
6. Biesenberger, J.A. and Sebastian, D.H., *Principles of Polymerization Engineering*, New York: Wiley, 1983.
7. Mamzurin, B.V., *Cand. Sci. (Chem.) Dissertation*, Moscow: Mendeleev Inst. of Chemical Technology, 1981.
8. Lebedev, N.N., Mamzurin, B.V., and Savel'yanov, V.P., *Zh. Org. Khim.*, 1985, vol. 55, p. 543.