React. Kinet. Catal. Lett., Vol. 47, No. 1, 51-57 (1992)

RKCL 1088

A METHOD FOR THE TREATMENT OF EXPERIMENTAL DATA. KINETIC SYSTEM COMPRISING TWO IRREVERSIBLE FIRST ORDER CONSECUTIVE REACTIONS

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Received September 18, 1991
Accepted November 25, 1991

A method is proposed for the treatment of data from a kinetic system comprising two irreversible first order consecutive reactions (A → B → C). It is based on the solving of contrary propositions for an ordinary differential equation.

Предложен метод обработки кинетических данных системы двух необратимых последовательных реакций первого порядка (A → B → C). Он основан на решении противоположных допущений обычного дифференциального уравнения.

INTRODUCTION

Alcock et al. [1] have described a compouter program for least-squares analysis of spectrophotometric data from a kinetic system comprising two irreversible first order consecutive reactions. It is based on the nonlinear Gauss-Newton method. Nevertheless, as pointed out by these authors, to perform the treatment successfully, it is essential that the initial estimates of parameters must not be too far from the correct values; otherwise the least-squares refinement may oscillate rather than converge (this difficulty can be alleviated but not eliminated by using Marquardt's algorithm [2]). If k_1 and k_2 are nearly equal, the least-squares refinement may oscillate between two solutions and never converge. Jackson et al. [3] have also considered the general problem of determining rate constants for consecutive reactions. Recently, Casado et al. [4] described a method for the treatment of data from a kinetic system comprising two irreversible first order consecutive reactions by using an optimization procedure. However, these methods are only applicable to the case of $k_1 \neq k_2$, and the initial estimates of parameters still need to be assumed.

In this paper, a new computational algorithm is intoduced. It is based on the solving of contrary propositions for an ordinary differential equation [5]. This analytical method circumvents the need for iterative operations, and no assumptions have been made concerning the initial estimates of the rate parameters.

THEORETICAL CONSIDERATIONS

Consider a kinetic system comprising two irreversible first order consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The kinetic equation is given be

$$C = A_o [1 + k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)]/(k_2 - k_1) \qquad (1)$$

where A_o is the initial concentration of A, and we assume that $B = C = 0$ when $t = 0$. If $k_1 = k_2$, eq. 1 is indeterminate and must be replaced by

$$C = A_o\ [1 - (kt - 1)\ \exp\ (-kt)] \tag{2}$$

here $k = k_1 = k_2$. The 1th and 2th derivatives of C with respect to t can be obtained from eq. 1

$$C' = -A_o[k_1k_2\ \exp(-k_2t) - k_kk_2\ \exp(-k_1t)]/(k_2 - k_1) \tag{3}$$

$$C'' = A_o\ [k_1k_2^2\ \exp(-k_2t) - k_1^2k_2\ \exp(-k_1t)]/(k_2 - k_1) \tag{4}$$

Let $\alpha = k_1 + k_2$, $\beta = k_1 + k_2$, and we can write the following ordinary differential equation

$$C'' + \alpha C' + \beta(C - A_o) = 0 \tag{5}$$

where α and β are unknown constants that must be determined from the nature of the experiment, that is, they are only determined by experimental data (C_i, t_i), $t_i = t_o + ih$, $i = 0,1,2,\ldots,n + 1$, and t_o is the initial sampling time, h is sample step. Thus, for determination of the kinetic parameters k_1 and k_2, it is necessary to solve eq. 5, which is contrary proposition for an ordinary differential equations. Let us take discretization for the ordinary differential equation: let $\Delta C_i = C_{i+1} - C_{i-1}$, $\Delta^2C_{i-1} = C_{i+1} - 2C_i + C_{i-1}$, thus α and β can be determined by the following overdetermined linear equation set

$$\Delta^2C_{i-1} + \alpha h\Delta C_i/^2 + \beta h^2(C_i - A_o) = 0, \quad i = 1,2,\ldots,n \tag{6}$$

The overdetermined linear equation set is most easily solved in terms of the least-squares method, that is, the following equation holds

$$Q(\alpha,\beta) = \sum_{i=1}^{n} (\Delta^2 C_{i-1} + \alpha h \Delta C_i/2 + \beta h^2 (C_i - A_o))^2 = \min \qquad (7)$$

Let $(\partial Q/\partial\alpha) = 0$, $(\partial Q/\partial\beta) = 0$ and solve the simultaneous equations, so α and β can be determined. From the definition of α and β, the rate constants, k_1 and k_2, may be determined directly.

From eq. 5 and the definition of α and β one can see that eq. 2 is also a solution for this ordinary differential equation (in this situation, $k=k_1=k_2$, $\alpha=2k$ and $\beta=k^2$). Thus, the new algorithm still applies for the case of $k_1=k_2$ and other methods would diverge for this situation.

Alternatively, the kinetic equation can be put into the form (let B=C=0, A=1 when t=0 and $k_1 \neq k_2$):

$$B = k_1 [\exp(-k_2 t) - \exp(-k_1 t)]/(k_1 - k_2) \qquad (8)$$

or in terms of the variable D representing the variations in optical density of the solution in a given time [1]

$$D = (\varepsilon_A - \varepsilon_C) \exp(-k_1 t) + k_1(\varepsilon_B - \varepsilon_C) (\exp(-k_2 t) - \exp(-k_1 t))/(k_1 - k_2 + \varepsilon_C \qquad (9)$$

where ε_A, ε_B, ε_C are the molar extinction coefficients of A, B and C, respectively. Under these circumstances, one might obtain $B''+(k_1+k_2)B'+k_1k_2(B-1)=0$ and $D''+(k_1+k_2)D'+k_1k_2(D-\varepsilon_C)=0$, they are again of the same form has equation 5, the preceding discussion again applies. In principle, so long as the kinetic equation has an exponential form, this analytical method becomes operative, and the rate constants k_1 and k_2 can be determined.

RESULTS AND DISCUSSION

According to this algorithm, a computer program that treats experimental data is readily written. We use the simulated data obtained with the arbitrary parameters to calculate the rate constants for consecutive reactions by this computer program. Results of the calculations are compared with theoretical values in Table 1. It may be seen that the agreement is quite good.

Table 1

Comparison of calculated results with theoretical values

theoretical		calculated	results		
k_1^*	k_2^*	k_1	$(k_1-k_1^*)/k_1^*100\%$	k_2	$(k_2-k_2^*)/k_2^*100\%$
500	5	500.8	0.16	4.992	-0.16
5	0.1	4.973	-0.55	0.100	-
0.05	0.01	0.04999	-0.02	0.0100	-
0.02	0.5	0.01999	-0.05	0.50003	0.006
5	5	4.997	-0.07	4.997	-0.07
0.005	0.005	0.004999	-0.02	0.004999	-0.02
0.045	0.05	0.04515	0.34	0.0498	-0.40

To obtain k_1 and k_2, it is necessary to calculate the value of $(\alpha^2-4\beta)^{1/2}$ when this computer program is used for data processing. Since $\alpha^2-4\beta\equiv(k_1-k_2)^2$, it must be true that $\alpha^2-4\beta\geqq 0$. However, if k_1 and k_2 are nearly equal, the case of $\alpha^2-4\beta<0$ may appear to take account of the error (for example, error of measurement or error of calculation). In program design, the problem can be solved to any desired accuracy. Tables 2 and 3 show the effect of the sample size (n) and the sample step (h) on the analytical results from the new algorithm (assuming that the change in concentration of B is measured and let $k_1^x = 0.05\ s^{-1}$, $k_2^* = 0.2\ s^{-1}$).

Table 2

Effect of sample size (n) on the results (let h=0.01 s)

n	k_1	$(k_1-k_1^*)/k_1^*100\%$	k_2	$(k_2-k_2^*)/k_2^*100\%$
5	0.05299	6	0.0944	-6
7	0.04968	-0.64	0.1006	0.64
9	0.05023	0.46	0.09954	-0.47
15	0.04993	-0.14	0.10013	0.14
21	0.04998	-0.04	0.10004	0.04

Table 3

Effect of sample step (h) on the results (let n=9)

h/s	k_1	$(k_1-k_1^*)/k_1^*100\%$	k_2	$(k_2-k_2^*)/k_2^*100\%$
0.01	0.05023	0.47	0.09954	-0.47
0.05	0.05001	0.02	0.09999	-0.01
0.10	0.049999	-0.002	0.10000	-
1.0	0.05005	0.10	0.09967	-0.33
10.0	0.05148	3	0.09187	-8

It may be seen that the algorithmic reliability is clearly quite good and n or h can be judiciously chosen so that better results should be obtained.

REFERENCES

1. N.W. Alcock, D.J. Benton, P. Moore: Trans. Faraday Soc., 66, 2210 (1970).
2. D.W. Marquardt: J. Soc. Ind. Appl. Math., 11, 431 (1963).
3. W.G. Jackson, J.M. Harrowfield: Int. J. Chem. Kinet., 9, 535 (1977).
4. J. Casado, J.I. Gonzalez, M.N. Moreno: React. Kinet. Catal. Lett., 33, 357 (1987).
5. Huang Youqian: Numerical Expression and Approximation for Curve and Surface, Chapter 2. Shanghai Scientific Press, Shanghai 1981.