

A METHOD FOR ESTIMATION OF KINETIC PARAMETERS; A SIMPLE FIRST-ORDER REACTION AND TWO PARALLEL FIRST-ORDER REACTIONS PRODUCING A COMMON PRODUCT

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A method is proposed for the treatment of data from a kinetic system of a simple first-order reaction and two parallel first-order reactions, producing a common product. It is based on the solving of a contrary proposition for an ordinary differential equation.

The nonlinear Gauss–Newton method is widely used for obtaining kinetic parameters from concentration (or other parameter) – time data, and the data treatment is usually done by a microcomputer¹. However, the use of this method for the treatment of experimental data is associated with a serious drawback, unless the initial parameter estimates are fairly close to the true values, the standard nonlinear least-squares techniques may diverge. This difficulty can be alleviated but not eliminated by using Marquardt's algorithm². The inherent weakness of the method is that the long-range convergence is not good enough. This difficulty can be overcome by using a new computational algorithm, which is based on the solving of a contrary proposition for an ordinary differential equation³. In this analytical approach, no assumptions are made concerning the initial estimates of the rate parameters, and it circumvents the need for iterative operations. It is clear that this analytical method does not suffer from the problem that nonlinear least-squares techniques may diverge.

In this paper we summarize the basic principle of the analysis method, considering two types of reactions: a) a simple first-order reaction ($A \xrightarrow{k} B$), and b) two parallel first-order reactions producing a common product ($A \xrightarrow{k_1} C$, $B \xrightarrow{k_2} C$).

THEORETICAL

Simple First-Order Reaction

The gas-phase decomposition reactions of di-*t*-butyl peroxide and chlorocyclohexane

have been studied by Raley and coworkers⁴ and by Swinbourne⁵, respectively. These are first-order reactions, examined by measuring the total pressure. The kinetic equation is

$$P(t) = P_{\infty} - (P_{\infty} - P_0) \exp(-kt), \quad (1)$$

where P_0 is initial pressure and P_{∞} is final pressure. The first derivative of $P(t)$ with respect to t can be obtained from Eq. (1) as

$$P'(t) = k(P_{\infty} - P_0) \exp(-kt). \quad (2)$$

Let $\alpha = k$, $\beta = -kP_{\infty}$; then we can write the following ordinary differential equation

$$P'(t) + \alpha P(t) + \beta = 0, \quad (3)$$

where α and β are unknown constants that must be determined from the experiment, because they are only determined by experimental data $(P(t_j), t_j)$ where $t_j = t_0 + jh$, $j = 0, 1, 2, \dots, m+1$, t_0 is the initial sample time and h is the sample step. Thus, for determination of the kinetic parameter k , contrary proposition has to be solved for the ordinary differential equation

$$P'_j + \alpha P_j + \beta = 0; \quad P_j = P(t_j), \quad j = 0, 1, 2, \dots, m+1. \quad (4)$$

Let us take discretization for the differential equation: let $\Delta P_j = P_{j+1} - P_{j-1}$, thus α and β can be determined from the overdetermined linear equation set

$$\Delta P_j/2h + \alpha P_j + \beta = 0, \quad j = 1, 2, 3, \dots, m. \quad (5)$$

This set is most easily solved by using the least square method; that is, the following equation is considered:

$$Q(\alpha, \beta) = \sum_{j=1}^m (\Delta P_j/2h + \alpha P_j + \beta) = \min. \quad (6)$$

Since there are two parameters involved, differentiation gives two normal equations:

$$\left. \begin{aligned} (\partial Q/\partial \alpha)_\beta &= 2 \sum_{j=1}^m (\Delta P_j/2h + \alpha P_j + \beta) P_j = 0 \\ (\partial Q/\partial \beta)_\alpha &= 2 \sum_{j=1}^m (\Delta P_j/2h + \alpha P_j + \beta) = 0 \end{aligned} \right\}. \quad (7)$$

The solutions of Eq. (7) give for α and β

$$\alpha = \frac{m \sum_{j=1}^m \Delta P_j P_j - \sum_{j=1}^m \Delta P_j \sum_{j=1}^m P_j}{2h((\sum_{j=1}^m P_j)^2 - m \sum_{j=1}^m P_j^2)} \quad (8)$$

$$\beta = \frac{\sum_{j=1}^m \Delta P_j P_j \sum_{j=1}^m P_j - \sum_{j=1}^m \Delta P_j \sum_{j=1}^m P_j^2}{2h(m \sum_{j=1}^m P_j^2 - (\sum_{j=1}^m P_j)^2)} \quad (9)$$

Once α and β have been evaluated, the k and P_∞ values can be determined directly, without iterative computation. A computer program that treats experimental data is readily written from the algorithm. It is clear that this algorithm does not require any assumption about the initial estimates of the kinetic parameters. This method has another advantage, viz. that the final pressure P_∞ need not be known (the determination of the final pressure would require an excessively long time).

Two Parallel First-Order Reactions Producing a Common Product

The hydrolysis of mixed tertiary aliphatic chlorides has been studied by Brown and Fletcher⁶. The kinetic equation is

$$C(t) = C_\infty - A_0 \exp(-k_1 t) - B_0 \exp(-k_2 t), \quad C_\infty = A_0 + B_0. \quad (10)$$

To obtain k_1 and k_2 , Brown and Fletcher used a logarithmic expression. If there is just one reaction A or B , or if $k_1 = k_2$, the plot of $\lg(C_\infty - C)$ versus t is linear. If, on the other hand, both A and B occur and $k_1 \neq k_2$, the $\lg(A + B)$ or $\lg(C_\infty - C)$ versus t plot is a curve. The graphical methods are applied to obtain the rate constants from the concentration - time data. The rate constants k_1 and k_2 can also be calculated using the nonlinear Gauss-Newton method. By the method proposed in this paper the experimental data are handled more conveniently, and this is facilitated by the availability of microcomputers for data processing and acquisition. Let $\alpha = k_1 + k_2$, $\beta = k_1 \cdot k_2$; Eq. (10) shows that the contrary proposition for the ordinary differential equation which needs to be solved can be written as

$$C_j'' + \alpha C_j' + \beta(C_\infty - C_j) = 0, \quad C_j = C(t_j), \quad j = 0, 1, 2, \dots, m+1. \quad (11)$$

Let us take discretization for the ordinary differential equation, that is, let $\Delta^2 C_{j-1} = C_{j+1} - 2C_j + C_{j-1}$, $\Delta C_j = C_{j+1} - C_{j-1}$; thus α and β can be determined by the least-squares method. From the definition of α and β , the rate constants k_1 and k_2 can be determined directly.

RESULTS AND DISCUSSION

The experimental data of Swinbourne⁵ were employed to calculate the first-order rate constant k and final pressure P_∞ by the method proposed in this paper. A rate constant of $5.36 \cdot 10^{-4} \text{ s}^{-1}$ and a final pressure of 430.5 Torr were obtained. These are in a good agreement with the values of $5.38 \cdot 10^{-4} \text{ s}^{-1}$ and 430 Torr reported

by Swinbourne⁵. Fig. 1 summarizes the experimental results⁵ and calculated values. An even better fit can be obtained by our method.

From Eqs (8) and (9), it is clear that all of these expressions are indeterminate if $P(t_j)$ is constant. In this case the experimental method can be incorrect (no experimental manifestations can be seen), or no kinetic process occurs (the systems are in equilibrium).

From the data of Brown and Fletcher⁶ we calculated the rate constants k_1 and k_2 by the method proposed in this paper and by the nonlinear Gauss–Newton method. The results obtained are given in Table I and Fig. 2. They demonstrate that our method is more convenient than the nonlinear Gauss–Newton method (even the initial estimates are rather close to the true values).

From Eq. (11) we note that the algorithm applies for the case of $k_1 = k_2$, while the nonlinear Gauss–Newton method diverges. In addition, when treating experimental data by our method, a recursion formula can be given and the sample step and sample size can be judiciously chosen, owing to which better results can be obtained.

TABLE I
Comparison of results of different treatment

Treatment	k_1, h^{-1}	k_2, h^{-1}
Data of Brown	0.38	1.58
Our method	0.389	1.49
Nonlinear Gauss–Newton method	0.377	1.85

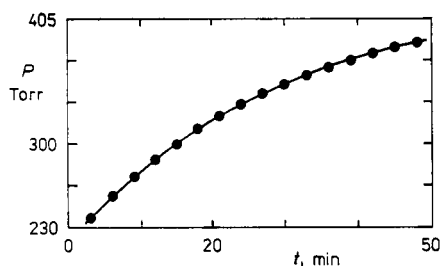


FIG. 1
Time dependence of pressure for thermal decomposition of chlorocyclohexane at 641 K; experimental data of Swinbourne⁵

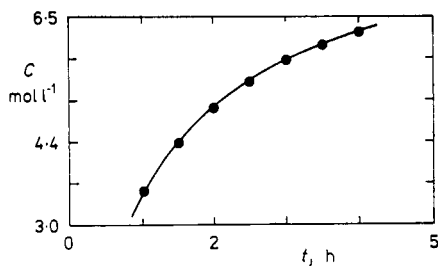


FIG. 2
Time dependence of concentration for the hydrolysis of diethylbutylcarbinyl chloride; experimental data of Brown⁶

REFERENCES

1. Moore J. W., Pearson R. G.: *Kinetic and Mechanism*. Wiley, New York 1981.
2. Marquardt D. W.: *J. Soc. Ind. Appl. Math.* *11*, 431 (1963).
3. Huang Youqian: *Numerical Expression and Approximation for Curve and Surface*, Chapter 2. Shanghai Scientific Press, Shanghai 1981.
4. Raley J. H., Rust F. F., Vaughn W. E.: *J. Am. Chem. Soc.* *70*, 88 (1948).
5. Swinbourne E. S.: *Aust. J. Chem.* *11*, 314 (1968).
6. Brown H. C., Fletcher R. S.: *J. Am. Chem. Soc.* *71*, 1845 (1949).

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