[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF NEBRASKA AND NORTHWESTERN UNIVERSITY]

A Numerical Method for the Kinetic Analysis of Two Consecutive Second Order Reactions

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A numerical method is presented for obtaining rate constants for two consecutive second order reactions. The method is illustrated by applying it to rate data for the saponification of ethyl adipate. The method should be applicable to most two step complex reactions.

Introduction

The use of numerical analysis[1a,2,3] of experimental data has found little favor among chemists even though it is a much more powerful tool than the commonly used graphical methods. It is the purpose of this paper to show how numerical differentiation and integration of rate data leads to the determination of rate constants for two consecutive second order reactions.

This type of complex reaction has been studied by a number of investigators[4,5,6] to determine rate constants for the saponification of esters of symmetrical dibasic carboxylic acids. These investigators all determined the second rate constant by a study of the rate of saponification of the half-ester. The first rate constant was then determined by various approximation methods.

An exact method of solution for this type of complex reaction has been formulated by the authors and will be published in the near future. However, this method suffers from the disadvantage that it is only applicable to the special case of stoichiometrically equivalent concentrations of the reacting substances.

Theory

The chemical equations and concentration variables for this system are

$$\begin{array}{lccccc} & A & + & B & \xrightarrow{k_1} & C \\ & A & + & C & \xrightarrow{k_2} & D \\ t = 0 & a & & b & & 0 \\ t: & x & & y & & x - 2y - (a - 2b) \end{array}$$

The rate equations are

$$dx/dt = -k_1xy - k_2x[x - 2y - (a - 2b)] \qquad (1)$$

$$dy/dt = -k_1xy \qquad (2)$$

If two new variables

$$\theta_i = \int_0^{t_i} xdt$$

$$\Phi_i = \left(\frac{d_0 \ln x}{dt}\right)_{t = t_i}$$

are introduced, the solution of equation (2) is

$$y_i = be^{-k_1\theta_i} \qquad (3)$$

The result of substituting this value of y in the equation (1) is

$$\Phi_i = -k_1be^{-k_1\theta_i} - k_2[x_i - 2be^{-k_1\theta_i} - (a - 2b)] \qquad (4)$$

This equation can then be solved for k_2.

$$k_2 = -\frac{\Phi_i + k_1be^{-k_1\theta_i}}{x_i - 2be^{-k_1\theta_i} - (a - 2b)} \qquad (5)$$

It is obvious that if two values of θ_i and Φ_i can be found, then there would exist two simultaneous equations in the unknowns k_1 and k_2. This set of equations could either be solved by eliminating k_2 between the equations and solving for k_1 by Newton's method; or graphically by plotting k_1 *vs.* k_2 for each equation, the intersection of the two curves giving the true values of k_1 and k_2. In practice, it is better to find three or more values of θ_i and Φ_i so that average values of k_1 and k_2 can be found. An approximate value of k_1 is readily determined, since

$$k_1 = -\left(\frac{d \ln x}{dt}\right)_{t = 0} \Big/ b \qquad (6)$$

Numerical Analysis and Results

Since, in general, it is not possible to obtain rate data at equal intervals of concentration, it is necessary to use Lagrange's formula for integration and differentiation. If $f(x)$ has the values $f(a_0)$, $f(a_1)$, $f(a_2) \cdots f(a_n)$ for values of $x = a_0, a_1, a_2 \cdots a_n$, then the nth degree polynomial passing through all of these points is given by

$$\begin{aligned} f(x) = {} & \frac{(x - a_1)(x - a_2)\cdots(x - a_n)}{(a_0 - a_1)(a_0 - a_2)\cdots(a_0 - a_n)} f(a_0) \\ & + \frac{(x - a_0)(x - a_2)\cdots(x - a_n)}{(a_1 - a_0)(a_1 - a_2)\cdots(a_1 - a_n)} f(a_1) \\ & \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ & + \frac{(x - a_0)(x - a_1)\cdots(x - a_{n-1})}{(a_n - a_0)(a_n - a_1)\cdots(a_n - a_{n-1})} f(a_n) \end{aligned}$$

This expression is readily differentiated and integrated.

The number of points to be used can be readily ascertained by considering the divided differences of the data. For the data considered here, it was found that a three-point formula was sufficient for the determination of Φ_i, using t_i as the middle point. The integration was performed using as many points as were in the interval considered, the value of θ_i being found by the sum of these intervals.

The data presented here are for the saponification of ethyl adipate at 25.00° in a water–dioxane solvent containing 25% dioxane by volume and made 0.2000 N in potassium chloride. The experimental details will be presented in the previously men-

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[4] C. K. Ingold, *J. Chem. Soc.*, 2170 (1931).

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tioned paper by the authors. Although these data are for the special case of $a - 2b = 0$, they have the advantage that the rate constants have been determined by an exact method.

Table I gives the values of x, t, Φ_i and θ_i.

TABLE I

RATE DATA FOR THE SAPONIFICATION OF ETHYL ADIPATE

a = initial concn. of sodium hydroxide = 0.00902 mole liter^{-1}. b = initial concn. of ethyl adipate = 0.00451 mole liter^{-1}

x = [NaOH] mole liter^{-1}	Time, seconds	$\Phi_i = \left(\frac{d \ln x}{dt}\right)_{t=t_i}$ seconds^{-1} $\times 10^{-4}$	$\theta_i = \int_0^{t_i} x dt$ liter^{-1} mole sec.
0.00902	0	−3.98	0
.00849	161		
.00808	309		
.00768	460		
.00724	655	−2.91	5.275
.00684	860		
.00650	1056		
.00604	1359	−2.32	9.922
.00565	1660		
.00531	1956		
.00501	2259	−1.83	14.863
.00468	2658		
.00431	3161		
.00401	3659	−1.42	21.122
.00374	4158		
.00352	4660		

The above information gives four equations of type (5). These equations were solved by elimination of k_2 between successive pairs of equations and the use of Newton's method.

Table II gives the values of k_1 and k_2 for the six possible cases.

TABLE II

k_1 liter mole^{-1} sec.$^{-1}$	k_2 liter mole^{-1} sec.$^{-1}$
0.0852	0.0309
.0857	.0301
.0850	.0312
.0870	.0297
.0849	.0312
.0812	.0318
Av. k_1 = 0.0848	Av. k_2 = 0.0308

The average values of k_1 and k_2 found by the exact method are

k_1 = 0.0855 liter mole^{-1} sec.$^{-1}$
k_2 = 0.0305 liter mole^{-1} sec.$^{-1}$

Conclusions

It is apparent that the numerical method used should be applicable to most two-step complex reactions. Further it can be used advantageously even in those cases where a closed form solution is known, since evaluation of rate constants is still a very tedious process in these cases.

Perhaps the chief disadvantage of the method is that rather precise data are necessary since values of k_1 and k_2 were found to be very sensitive to small errors in θ_i and Φ_i.

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Four Mechanisms Involving Nitrogen Pentoxide

BY HAROLD S. JOHNSTON

The mechanisms of four kinetic systems involving nitrogen pentoxide can be expressed in terms of eight reactions which are believed to be elementary steps. The central feature of these mechanisms is a rapidly attained equilibrium between nitrogen pentoxide and nitrogen dioxide and NO_3. In terms of the mechanism quantitative relations are found among the four systems. From experimental data plus two additional assumptions, seven out of eight rate constants and the equilibrium constant can be evaluated within one order of magnitude. The steady-state concentration of NO_3 can be estimated for each kinetic system. Approximate values of the energy of activation can be found for five of the eight steps.

Four complex kinetic systems, some of which have been extensively investigated, can be expressed in terms of eight processes which are believed to be elementary reactions. Some of these eight steps occur in all four mechanisms, and thus quantitative relations are to be sought between them.[1] The four kinetic systems are: (1) The decomposition of nitrogen pentoxide, (2) the decomposition of nitrogen pentoxide in the presence of nitric oxide, (3) the decomposition of ozone in the presence of nitrogen pentoxide, and (4) the formation of nitrogen pentoxide from ozone and nitrogen dioxide. The eight elementary steps are

$$N_2O_5 + M \xrightarrow{a_{iM}} N_2O_{5i}^* + M$$

$$N_2O_{5i}^* + M \xrightarrow{b_{iM}} N_2O_5 + M$$

$$N_2O_{5i}^* \xrightarrow{c_i} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{d_i} N_2O_{5i}^*$$

$$NO_2 + NO_3 \xrightarrow{e} NO + O_2 + NO_2$$

$$NO + NO_3 \xrightarrow{f} 2NO_2$$

$$NO_3 + NO_3 \xrightarrow{g} 2NO_2 + O_2$$

$$NO_2 + O_3 \xrightarrow{h} NO_3 + O_2$$

The asterisk denotes excitation, and the subscript i numbers the excited states of the nitrogen pentoxide above the critical energy. M denotes any gas molecule which contributes to the excitation and de-excitation of nitrogen pentoxide. The subscript M on the specific rate constants is necessary because the excitation and de-excitation rates depend on the nature of the gas M as well as on its concentration. If all gases are equally

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(1) H. S. Johnston, *The Vortex* **9**, 356 (1948); Thesis, Calif. Inst. of Tech., 1947.