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COMPUTERIZED ANALYSIS OF SINGLE DTA CURVE DATA BY A MULTIPLE LINEAR REGRESSION METHOD FOR THE EVALUATION OF NONISOTHERMAL KINETIC PARAMETERS

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ABSTRACT

It is well known that thermal analysis techniques are widely applied in the characterization of polymer cure and pyrolytic processes and in probing reaction kinetics. However, differential thermal analysis is frequently applied in researching nonisothermal reaction kinetics. In this work, the nonisothermal rate equation has been incorporated into a computer program which performs an automatic calculation of kinetic parameters by a multiple linear regression method from data for a single DTA curve. This computerized analysis is quite general and applied to various thermal events.

INTRODUCTION

The knowledge of reaction kinetics is important in two respects. First, such kinetics are related to simple mathematical descriptions of the process. Second, they are important data in the evaluation of stability and compatibility for energetic materials and in the study of manufacturing processes for crystalline materials. Since thermal analysis techniques show versatility in studying the kinetics of cases such as those of crystalline and non-crystalline materials, a number of methods for evaluating the kinetic parameters has been developed. Both isothermal and nonisothermal forms of the Johnson–Mehl–Avrami rate equation have also been explored. Various analysis methods have been employed, which include peak displacement [1–3], temperature integral [4], temperature derivation [5], combined differential and integral [6], and linear interpolation methods [7]. It is generally recognized that further studies of kinetic processes are necessary, meaningful and important.

In general, it is advantageous to determine kinetic parameters from a single curve analysis, especially if large amounts of materials are to be analyzed. In this paper, we create a computer program that is based on

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multiple linear regression analysis for evaluating the nonisothermal kinetic parameters from a single DTA curve. The analogue curve data of DTA are converted into digital curve data through the RS-232 serial interface card of a PC/AT microcomputer. The temperature displacements are functions of temperature and partial area in a reaction peak. A reaction peak can be divided into many small strips, the sets of data strips, $(X_i, T_i, \Delta T_i)$, being taken into the multiple linear regression program to calculate the activation energies and orders of the reaction. The computerized analysis system has been applied to the thermal decomposition processes of $NaHCO_3$ and $CaC_2O_4 \cdot H_2O$, and the calculated kinetic parameters are consistent with those in the literature. However, this analysis system offers the advantage of being straightforward for both data acquisition and analysis of kinetic parameters.

THEORETICAL

Kinetics

As in many nonisothermal kinetic investigations, we shall start from the fundamental differential rate equation

$$\mathrm{d}X/\mathrm{d}t = k(T)f(X) \tag{1}$$

where t indicates time, T is temperature, and X denotes degree of conversion. The dependence of reaction rates on temperature is usually assumed to be an Arrhenius type equation

$$k(T) = A\ \exp(-E/RT) \tag{2}$$

or the equation predicted by transition state theory

$$k(T) = AT^b \exp(-E/RT) \tag{3}$$

where E is the apparent activation energy, A is the pre-exponential factor, R is the gas constant, and b is a constant. It is worthwhile to mention that $k(T)$ simply represents the isothermal rate constant. As far as the conversion function is concerned, its general form is [8]

$$f(X) = (1-X)^n X^m [-\ln(1-X)]^p \tag{4}$$

where n, m and p are constants. Combining eqns. (1), (3) and (4), we have

$$\mathrm{d}X/\mathrm{d}t = AT^b \exp(-E/RT)(1-X)^n X^m [-\ln(1-X)]^p \tag{5}$$

Taking logarithms on both sides of eqn. (5)

$$\begin{aligned}\ln(\mathrm{d}X/\mathrm{d}t) = {} & \ln A + b \ln T - (E/R)(1/T) + n \ln(1-X) + m \ln X \\ & + p \ln[-\ln(1-X)]\end{aligned} \tag{6}$$

Equation (6) may be written in the following form

$$Y = A_0 + A_1 Z_1 + A_2 Z_2 + A_3 Z_3 + A_4 Z_4 + A_5 Z_5 \tag{7}$$

Multiple linear regression (MLR)

The techniques of least-squares fitting which have been developed [9] fall into the general category of regression analysis. Consider a general function which is linear in the coefficients

$$Y = A_0 + A_1 X_1 + A_2 X_2 + \ldots + A_n X_n \tag{8}$$

where the X_i are functions of independent variables and the A_i indicate coefficients. The method of least squares results in a set of $n+1$ simultaneous equations

$$\begin{aligned} \Sigma_i Y_i &= A_0 N + A_1 \Sigma_i X_1 + A_2 \Sigma_i X_2 + \ldots + A_n \Sigma_i X_n \\ \Sigma_i Y_i X_j &= A_0 \Sigma_i X_j + A_1 \Sigma_i X_1 X_j + A_2 \Sigma_i X_2 X_j + \ldots A_n \Sigma_i X_n X_j \end{aligned} \tag{9}$$

The sums are taken over the N observations, considering the X_j to be functions $X_j(x_i)$.

One can simplify these equations and increase their symmetry by considering the first equation to be a separable solution for the first term A_0 in the fitting function of eqn. (8). Rewriting the first equation of eqns. (9) in such a way that the coefficient A_0 is expressed explicitly as a function of all the other coefficients

$$\begin{aligned} A_0 &= (1/N)[\Sigma_i Y_i - A_1 \Sigma_i X_1 - A_2 \Sigma_i X_2 - \ldots - A_n \Sigma_i X_n] \\ &= \overline{Y} - A_1 \overline{X}_1 - A_2 \overline{X}_2 - \ldots - A_n \overline{X}_n \end{aligned} \tag{10}$$

where $\overline{Y}$ and $\overline{X}_j$ are averages of Y_i and the functions $X_j(x_i)$ over the N observations. After solving the remaining n simultaneous equations, one can then substitute the fitted values of the n coefficients A_j into eqn. (10) to solve the constant coefficients A_0.

With the definition, the formula for χ^2 becomes

$$\begin{aligned} \chi^2 = (1/\sigma^2)\Sigma_i \big[(Y_i - \overline{Y}) - A_1 (X_1 - \overline{X}_1) - A_2 (X_2 - \overline{X}_2) \\ - \ldots - A_n (X_n - \overline{X}_n) \big]^2 \end{aligned} \tag{11}$$

The values of the coefficients for which χ^2 is a minimum are determined by setting the derivatives of χ^2 with respect to each of the n coefficients A_j equal to 0. This yields n simultaneous equations.

$$\Sigma_i (Y_i - \overline{Y})(X_k - \overline{X}_k) = \Sigma_j^n \big[A_j \Sigma_i (X_j - \overline{X}_j)(X_k - \overline{X}_k) \big] \quad k = 1 \text{ to } n \tag{12}$$

These equations can be simplified further by substituting the definitions for the linear correlation coefficients r_{ij} given as follows

$$r_{jk.} = s_j k^2/(s_j s_k),\ r_{jy} = s_{jy}^2/(s_j s_y)$$

$$s_{jk}^2 = [1/(N-1)]\Sigma_i\left[\left(X_j - \overline{X}_j\right)\left(X_k - \overline{X}_k\right)\right]$$

$$s_{jy}^2 = [1/(N-1)]\Sigma_i\left[\left(X_j - \overline{X}_j\right)\left(Y_i - \overline{Y}\right)\right]$$

$$s_j^2 = [1/(N-1)]\Sigma_i\left(X_j - \overline{X}_j\right)^2$$

$$s_y^2 = [1/(N-1)]\Sigma_i\left(Y_i - \overline{Y}\right)^2 \qquad (13)$$

Equations (12) become n simultaneous equations in b_j

$$r_{ky} = \Sigma_j^n b_j r_{jk}\ \ k = 1 \text{ to } n \qquad (14)$$

where the coefficients b_j are related to the coefficients A_j of the function of eqn. (8)

$$b_j = A_j s_j / s_y \qquad (15)$$

and the diagonal terms in r are unity, $r_{jj} = 1$. Consider eqns. (14) to be a matrix equation

$$[r_y] = [r][b] \qquad (16)$$

here $[r_y]$ and $[b]$ are column matrices of linear correlation coefficients r_{jy} and coefficients b_j, and $[r]$ is the matrix of the linear correlation coefficients r_{ij}, for which the solution is

$$[b] = [r]^{-1}[r_y]$$

$$b_j = \Sigma k^n\left(r_{ky} r_{jk}^{-1}\right) \qquad (17)$$

where $r_{jk}^{-1} = r_{kj}^{-1}$ is the jth term of the matrix $[r]^{-1}$, which is the inverse of the matrix $[r]$ of the linear correlation coefficients.

The partial regression coefficients A_j of the original function of eqn. (8) can be determined by substituting the definition of eqn. (15)

$$A_j = \left(s_y/s_j\right)\Sigma k^n\left(r_{ky} r_{ik}^{-1}\right) \qquad (18)$$

EXPERIMENTAL

The measurements were carried out on a Rikagu–Denki differential thermal analyzer, model 8121. The heating rates applied were 5, 10 and 20 °C min^{-1}. The α-alumina powder was used as a reference material over all measurements. The measured materials ($NaHCO_3$, $CaC_2O_4 \cdot H_2O$) were used in powder form without further treatment.

In a regular run, the DTA curves of the decomposition process of the sample were collected on the DT analyzer. The analogue signals of the DTA curve were transferred to a fully IBM compatible PC/AT by a RS-232 interface system, and were converted into digital data and saved in a disk file. A set of data for a reaction peak can be located from the disk file and loaded into the MLR program to be analyzed.

DATA ANALYSIS AND RESULTS

Consider the characteristic temperature of the DTA curve in Fig. 1. The temperature deviation ΔT from the DTA baseline will be proportional to the reaction rate of the material [10]

$$\Delta T = K(\mathrm{d}X/\mathrm{d}t) \tag{19}$$

where K is a constant. Here the rate of the decompositional process is expressed by

$$\mathrm{d}X/\mathrm{d}t = A(1-X)^n \exp(-E/RT) \tag{20}$$

Combining eqns. (19) and (20), we have

$$\Delta T = (A/K)(1-X)^n \exp(-E/RT) \tag{21}$$

Taking logarithms of eqn. (21), one can obtain a formula similar to eqn. (6)

$$\ln \Delta T = \ln(A/k) + n \ln(1-X) - (E/R)(1/T) \tag{22}$$

However, we can take a set of data, (X_i, T_i, ΔT_i), from the DTA curve into eqn. (22) to be calculated, and evaluate the activation energy and reaction order.

The reaction of dehydration of calcium oxalate monohydrate and the reaction of decarboxylation of sodium bicarbonate have been studied by DTA. The obtained data were processed by our programs. The results

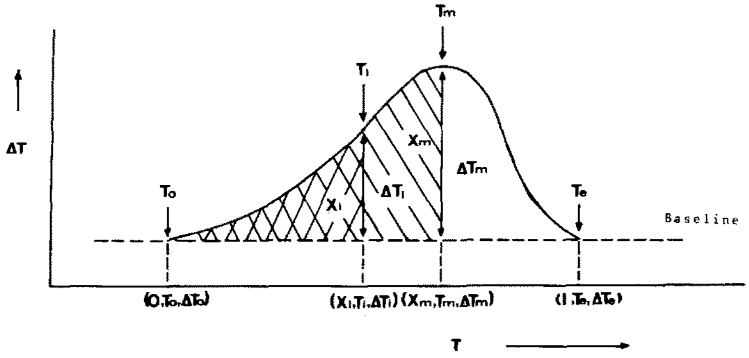

Fig. 1. The characteristic temperature of the DTA curve.

TABLE 1

Kinetic parameters of thermal decomposition materials

Compound	Values calc. in this work		Literature values		Ref.
	n	E (kcal mol^{-1})	n	E (kcal mol^{-1})	
$NaHCO_3$	1.01	19.5	0.90	22.4	10
			0.77–0.78	22–23	11
			0.83	22–24	12
$CaC_2O_4 \cdot H_2O$	0.71	27.2	0.71	13.2	10
			0.98	22	12
			1.0	20.8	13

calculated are listed in Table 1, and show a good agreement with those found in the literature [10–13]. The amount of sample and the heating rate do not influence the values of the kinetic parameters.

CONCLUSIONS

1. A multiple linear regression program has been created which enables direct simulation of the curve data of DTA without complicated mathematical transformation.
2. The program can also be applied to analyze the reaction kinetics of other thermal analysis techniques, such as DSC curves.
3. This work offers a simplified and convenient method for rapidly calculating kinetic parameters.

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