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TWO NEW METHODS FOR CALCULATION OF KINETIC PARAMETERS FROM THERMOGRAVIMETRIC DATA

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ABSTRACT

This paper presents two new methods of calculation of the kinetic parameters. One of them is established by steepest descent iterative procedure and another one by direct computing procedure. Both methods are suitable for on-line operation with computer and may provide all kinetic parameters (n, E, A) completely in one and five minutes respectively without trial and error procedure on the IBM-PC microcomputer.

INTRODUCTION

Suppose the reaction considered is in the liquid or solid state. In the course of reaction, suppose one substance has volatilized, the others are in the state of coacervation. The reaction can be expressed in the following form

$$a\,A\,(s) \xrightarrow{\text{heated}} b\,B\,(s) + c\,C\,(g)$$

If the experiment in which the temperature is increasing at linear speed, the reaction meets the following kinetic equations:

$$\begin{cases} -\dfrac{d\alpha}{dt} = K\,(1-\alpha)^n \\ K = A\exp(-E/RT) \\ T = T_0 + \beta t \end{cases} \qquad (1)$$

in which α denotes the decomposition fraction of the reactart at t - moment, K the speed of decomposition, t the reactions time, T the absolute temperature, n the order of reaction, A the factor of frequency, E the reaction energy of activation, R the constant of gas, and β the speed of the rising temperature.

Suppose a set of observed values, (T_i, α_i), $i = 0,1,\cdots,m$, is randomly obtained from a TG curve. For calculating the kinetic parameter values of n, A and E, many scholars have made much progress

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on simplification and linearization handling for eq. (1) by different ways, but the computing precision looses too much although many simple and convenient computing formulae have been made. Moreover, for computing n, many calculation methods often are performed by the trial-and-error procedure under some certain assumption, in addition, these are not favourable to the automatic data processing in the thermogravimetric study. For these reasons, we propose the following two numerical methods.

NUMERICAL METHOD I

The algorithm given here is called iterative method

1. The principle of the method: From eq. (1) one has

$$\begin{cases} \alpha = 1 - \left[(1-\alpha_0)^{1-n} + \dfrac{(1-n)A}{\beta} I(E,T) \right]^{\frac{1}{1-n}}, & n \neq 1 \\ \alpha = 1 - \exp\left[\mathrm{Ln}(1-\alpha_0) + \dfrac{A}{\beta} I(E,T) \right], & n = 1 \end{cases} \tag{2}$$

Where $I(E,T) = \int_{T_0}^{T} \exp(-E/RT)\,dT$

It is obvious that expressions in (2) are nonlinear with respect to n, A and E. Without loss of generality, we assume that they are nonlinear functions including p parameters b_i, $(i=1,2,\cdots,p)$. Let

$$\alpha = g(T, b_1, b_2, \cdots, b_p) \tag{3}$$

If a set of initial data $b_i^{(o)}$, $(i=1,2,\cdots,p)$, of $b_i, (i=1,2,\cdots,p)$ are given, and denoted by $\Delta_i = b_i - b_i^{(o)}$, $i=1,2,\cdots,p$, the derivation from accurate values and the initial data, then one has

$$b_i = b_i^{(o)} + \Delta_i \qquad i=1,2,\cdots,p \tag{4}$$

Hence, the problem of solving for bi is changed into the problem of solving for Δ_i.

Making the Taylors expansion of eq. (3) in some neighborhood of $b_i^{(o)}$, and ignoring the terms of order of $\Delta_i \geqslant 2$, one gets

$$g(T_k, b_1, b_2, \cdots, b_p) \doteq g_{ko} + \frac{\partial g_{ko}}{\partial b_1}\Delta_1 + \cdots + \frac{\partial g_{ko}}{\partial b_p}, \tag{5}$$

where

$$g_{ko} = g(T_k, b_1^{(o)}, b_2^{(o)}, \cdots, b_p^{(o)}), \quad k=0, 1, 2, \cdots, m,$$

$$\frac{\partial g_{ko}}{\partial b_i} = \frac{\partial g(T,\ b_1,\cdots,b_p)}{\partial b_i}\Bigg|_{\substack{T=T_k \\ b_j=b_j^{(o)} \\ 1\leqslant j\leqslant p\ ,}} \qquad \begin{array}{l} k=0,\ 1,\ 2,\cdots,m \\ i=1,\ 2,\cdots,p\ . \end{array}$$

If replaced eq. (3) by eq. (5), the quadratic sum of residual errors could be expressed as

$$Q(b_1,b_2,\cdots,b_p)= \sum_{k=0}^{m}\left[\alpha_k-g(T_k,\ b_1,\cdots,b_p)\right]^2$$

$$\doteq \sum_{k=0}^{m}\left[\alpha_k-(g_{ko}+\frac{\partial g_{ko}}{\partial b_1}\Delta_1+\cdots+\frac{\partial g_{ko}}{\partial b_p}\Delta_p)\right]^2$$

According to the extremum principle, b_i, $(i=1,2,\cdots,p)$ are satisfied with the equations

$$\frac{\partial Q}{\partial b_i}=0\ ,\quad i=1,\ 2,\cdots,p \tag{6}$$

Assume that

$$a_{ij}=\sum_{k=0}^{m}\frac{\partial g_{ko}}{\partial b_i}\cdot\frac{\partial g_{ko}}{\partial b_j}$$

$$a_{i\alpha}=\sum_{k=0}^{m}\frac{\partial g_{ko}}{\partial b_i}(\alpha_k-g_{ko}) \qquad i,j=1,2,\cdots,p \tag{7}$$

Then eq. (6) can be converted into the following linear equations of Δ_i

$$\sum_{j=1}^{p}a_{ij}\,\Delta_j=a_{i\alpha},\quad i=1,2,\cdots,p \tag{8}$$

Thus Δ_i and b_i, $(i=1,\ 2,\cdots,p)$, can be calculated by eq. (7), (8) and eq. (4) provided $b_i^{(o)}$, $(i=1,\ 2,\cdots,p)$ are given.

If each Δ_i calculated is larger, we can replace $b_i^{(o)}$ by the new bi calculated and then make iterations until $\max\limits_{1\leq i\leqslant p}|\Delta_i|<\varepsilon$(the allowable precision) is satisfied.

However, the above iteration scheme is often not convergent because of omitting the terms with orders higher than 2 in Taylor expansion and inaccurate selection of the initial data $b_i^{(o)}$. For this it can be solved by increasing the diagonal elements of the coefficient matrix of eq. (8), and eq. (8) as

$$(a_{ii}+d)\,\Delta_i+\sum_{\substack{j=1\\ j\neq i}}^{p}a_{ij}\,\Delta_j=a_{i\alpha}\ ,\quad i=1,\ 2,\cdots,p\ . \tag{8$'$}$$

Where $d \geqslant 0$. It can be proved that the convergence of the iteration can be guaranteed if the selected d is large enough. Such a solution is still the solution of iteration in the steepest descent direction.

2.One should take the initial data $b_i^{(o)}$ as close to the exact values as possible, otherwise the convergence will be very slow or even not convergent. Besides, in the course of calculation tne coefficient matrix of eq. (8) is from time to time ill-conditioned. Therefore, some suitable process of coefficient matrix is necessary to be treated.

NUMERICAL METHOD II —DIRECT METHOD

We can also use the known data (T_i, α_i), $(i=0,1,2,\cdots,m)$ and make a suitable curve fitting for eq. (1) and then eq. (1) will be changed into the following equations

$$\sum_{j=1}^{3} a_{ij}\, b_j = a_{iy}\ , \quad i=1,2,3\ . \tag{9}$$

where

$$b_1=n, \quad b_2=\mathrm{Ln}A, \quad b_3=E \tag{10}$$

$$a_{ij}=a_{ji}=\sum_{k=0}^{m} c_{ik}c_{jk}\ , \quad a_{iy}=\sum_{k=0}^{m} c_{ik}y_k\ , \quad i,j=1,2,3. \tag{11}$$

$$\begin{cases} y_k=\mathrm{Ln}Q(T_k)+\mathrm{Ln}\beta, \quad c_{1k}=\mathrm{Ln}(1-\alpha_k) \\ c_{2k}=1\ , \quad c_{3k}=-\dfrac{1}{RT_k}\ , \\ (Q(T)\text{is the curve fitting function}) \end{cases} \tag{12}$$

Therefore the values of n, A and E can be easily obtained from eq. (9)-(12).

THE EXPERIMENTS AND THE RESULTS OF CALCULATION

All experiments were performed on the shimatzu DT-20B thermal analysis equipment. We first used the above methods to treat the TG data of the decomposition of calcium formate as the kinetic parameters were known from the literature.

We have made the Basic programme on IBM-pc and compared the calculated results with data collected from the literature (Table 1).

TABLE 1

Comparison of values of kinetic parameters from different sources for thermal decomposition of $CaC_2O_4\cdot H_2O$

The work		Freeman-Carroll$^{(1)}$	Coats$^{(2)}$	Gurrieri-Siracusa$^{(3)}$	Liu Jinxiang et al.$^{(4)}$	Meth.	
						1	2
A	E	22	21.4	21.1	20.55	15.04	15.04
	n	1	0.71		1	0.63	0.62
	A	$2.8\cdot10^6$			$2.43\cdot10^7$	$2.60\cdot10^6$	$2.58\cdot10^6$
B	E	74	62.0	73.5	65.13	61.74	61.74
	n	0.7	0.38		0.7	0.75	0.71
	A	$1.4\cdot10^{17}$			$7.27\cdot10^{15}$	$4.37\cdot10^{17}$	$4.37\cdot10^{17}$
C	E	39	51.7	40.9	54.30	48.04	48.43
	n	0.4			0.4	0.36	0.36
	A	$2.6\cdot10^9$			$7.14\cdot10^7$	$2.77\cdot10^8$	$3.25\cdot10^8$

DISCUSSION

1. Both methods avoid the trial-and-error procedure in calculating the order of reaction, and calculate all the kinetic parameters at one time. These methods are applicable for the automatic data processing on analytical apparatus. They can also be used for other formulae of kinetic function in principle.

2. The calculation velocities of the two methods are all rapid. It takes about five minutes and one minute, respectively, for method 1 and 2 to calculate the kinetic parameters of a step,However- method 2 is more convenient.

3. Also we can use method 2 first and work out the results which are then used as the initial data of method 1 to do the further iteration. The calculation precision will be more accurate if the two methods are used simultaneously.

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