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Computer kinetic analysis of thermoanalytical data

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Abstract

A program has been worked out to provide kinetic analysis of non-isothermal data. To evaluate the kinetic parameters the main procedure uses the integral method of exponential multipliers (IMEM). TG and DTA curves have been recorded with a Setaram TAG 24S24 thermoanalyser. The program has been tested for dehydration of $CaC_2O_4 \cdot H_2O$. Also it has been applied to the kinetic study of copper oxidation with barium peroxide and oxygen thermodesorption in $YBa_2Cu_3O_{6.9 \pm 0.1}$ superconductor.

INTRODUCTION

A great many recent articles have been devoted to programming of well-known methods which had been worked out between 1950 and 1960 [1–4]. The authors tried to put the treatment on a computer. To evaluate kinetic parameters they had to decrease the amount of input data, to smooth it, to take logarithms and then to use the least squares method. It seems to us that this traditional way of data processing forces an investigator to lose a great part of the information recorded with present day apparatus. To avoid this we chose IMEM[5] recently developed just for the computer kinetic analysis of non-isothermal data. We wrote conversational programs for treatment of TG and DTA curves in order to calculate the values of single- or double-stage process kinetic parameters. The conversational mode permits an investigator to control the sequence of processing. Input and output data are visualised. To demonstrate the computer run the program has been applied to kinetic analysis of calcium oxalate dehydration.

EXPERIMENTAL

A Setaram TAG 24S24 thermoanalyser was used for recording TG and DTA curves. The experiments were performed at linear heating with heating rates of 2.5 and 5 K min^{-1}, in both static air and flowing argon, by use of α-alumina as a reference material. In each measurement about 30

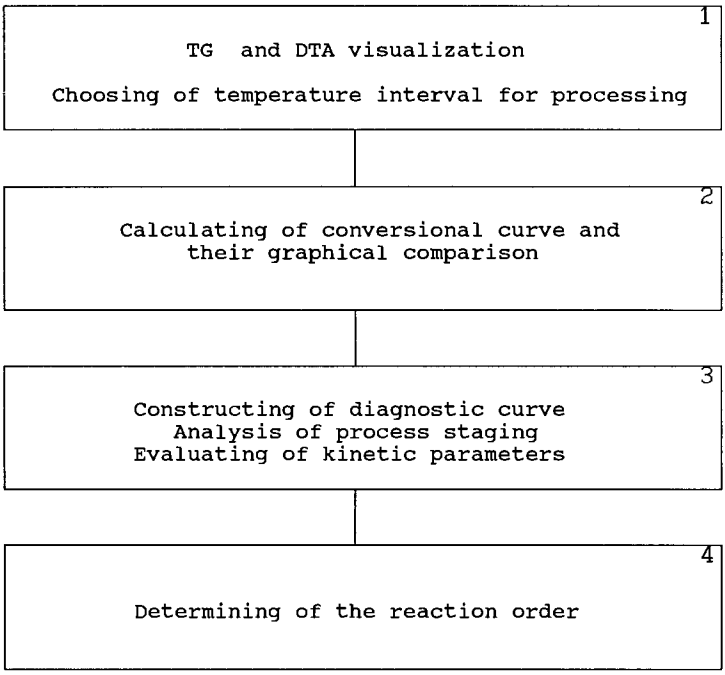

Fig. 1. The logical diagram for the computer program.

mg of specimen were weighed and about 5000 data concerning the weight loss and as many data concerning the heat flow were collected at regular intervals of time. The temperature (T) was recorded with an accuracy of ± 0.1 K.

DESCRIPTION OF THE PROGRAM

The logical diagram of the program is given in Fig. 1. Data concerning the temperature, weight loss and heat flow were collected in a file. The dependences of weight loss and heat flow upon temperature or time could be displayed on the screen by pushing certain functional buttons. The conversational sentences and prompts appear on the screen when necessary. At this point we could choose the kind of data for treatment (TG or DTA curve) and we could define the temperature interval and a whole curve or a part of it for evaluation procedure. Figure 2 demonstrates TG and DTA curves for calcium oxalate dehydration.

The next step is the calculation of the conversional curves (Fig. 1, block 2).

For thermogravimetry the formula is

$$\alpha_t = \frac{W_\infty - W_t}{W_\infty}$$

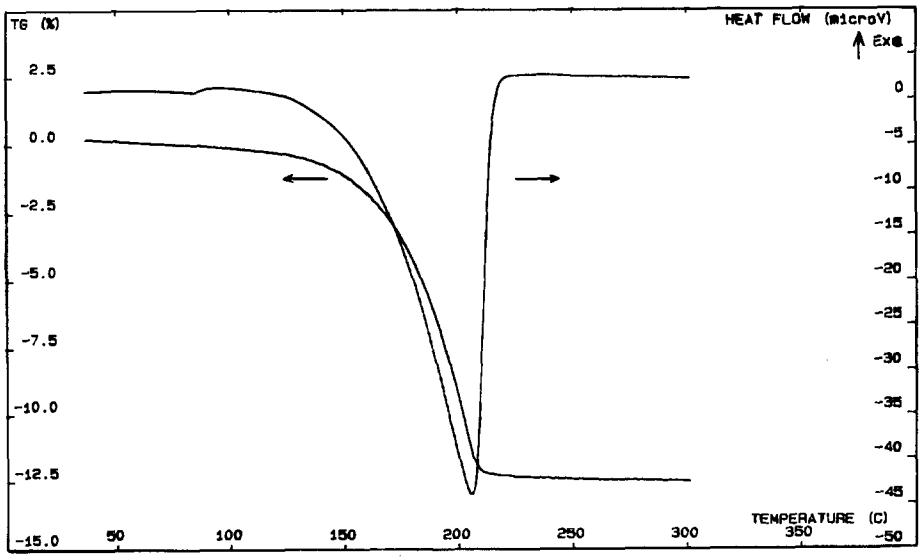

Fig. 2. Typical TG and DTA curves of calcium oxalate dehydration.

where W_∞ is the weight loss at the completion of the reaction, W_t is the weight loss up to time t, α_t is the degree of conversion up to time t.

For differential thermal analysis the formula is

$$\alpha_t = \frac{\int_0^{t_0} \dot{q}(\tau)\, \mathrm{d}\tau}{\int_0^{t_\infty} \dot{q}(\tau)\, \mathrm{d}\tau}$$

where $\dot{q}(\tau)$ is the value of the heat flow up to time t, α_t is the degree of conversion up to time t, and t_∞ is the time taken for reaction completion. The graphic comparison of these two curves makes it possible to conclude whether the weight loss and the change of heat flow depend on the same chemical process (Fig. 3).

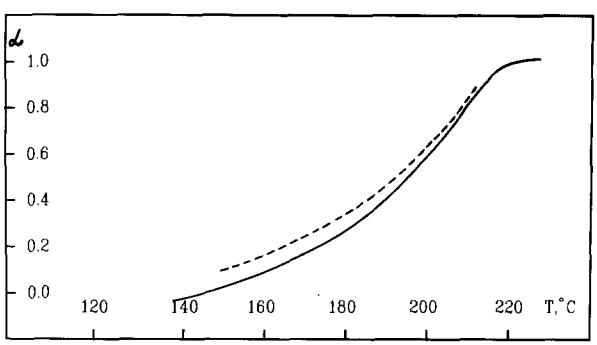

Fig. 3. Degree of conversion. Broken line, degree of conversion calculated from TG data; solid line, degree of conversion calculated from DTA data.

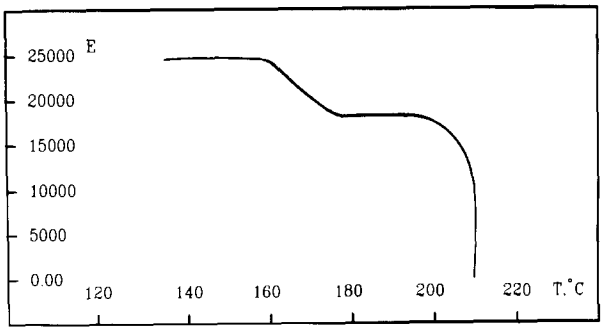

Fig. 4. Diagnostic curve.

The main procedure of the program is the construction of a "diagnostic" curve, examination of its shape and evaluation of kinetic parameters (Fig. 1, block 3). The integral method of exponential multipliers (IMEM) is applied to it. IMEM is an integral analog of MEM [6], more useful in practice than MEM. Observation of the diagnostic curve's shape gives us the opportunity to determine whether it is a single or multistage process, and also whether there is any part of the curve which corresponds to a single-stage process. For $CaC_2O_4 \cdot H_2O$ the diagnostic curve shows that the dehydration reaction is a single-stage process in the temperature interval 138–250°C. The beginning of the curve estimates the value of activation energy that equals 23 700 cal mol^{-1} (Fig. 4). The table displayed on the screen contains the values of degree of conversion, frequency factor, activation energy and its accuracy at certain small temperature intervals. The accuracy of activation energy depends upon the experimental error and the size of the temperature interval [5].

After estimation of kinetic parameters we may determine the reaction order. Figures 5–7 illustrate the search procedure for $CaC_2O_4 \cdot H_2O$. Putting any values of reaction order, we want the theoretical conversional

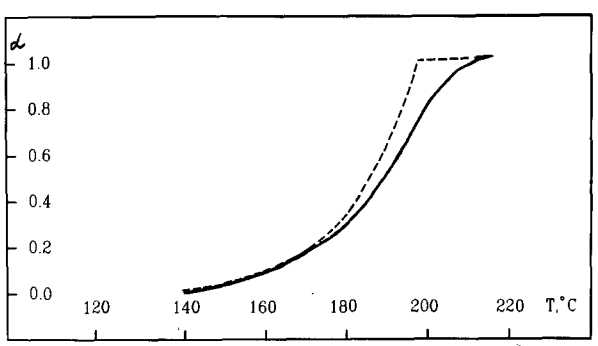

Fig. 5. Order of reaction $n = 0$. Broken line, theoretical degree of conversion as the solution of the kinetic equation; solid line, degree of conversion calculated from experimental data.

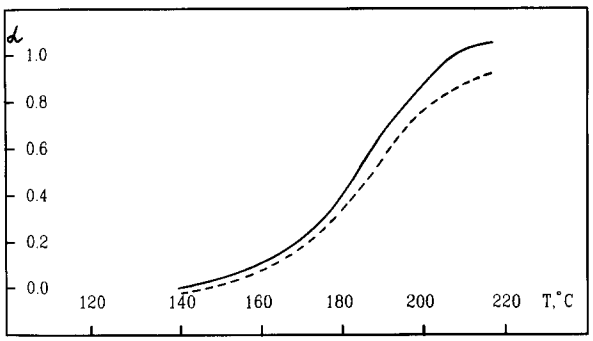

Fig. 6. Order of reaction $n = 1$. Broken line, theoretical degree of conversion as the solution of kinetic equation; solid line, degree of conversion calculated from experimental data.

curve to be in agreement with that of experiment. If the input value is correct we may observe a good correspondence between both curves (Fig. 7). This procedure is the last in the program (Fig. 1, block 4).

TABLE 1

Values of activation energy E (kcal mol^{-1}), frequency factor A (sec^{-1}) and reaction order n

References	E	A	n
Masuda et al. [8]	19.4	1.890×10^{9}	0.5
Urbanovici and Segal [7]	21.4	7.380×10^{7}	0.5
Ninan and Nair [10]	24.6	3.100×10^{11}	
Salvador et al. [9]	26.0	5.200×10^{12}	0.33
This work	23.75	4.709×10^{8}	0.5

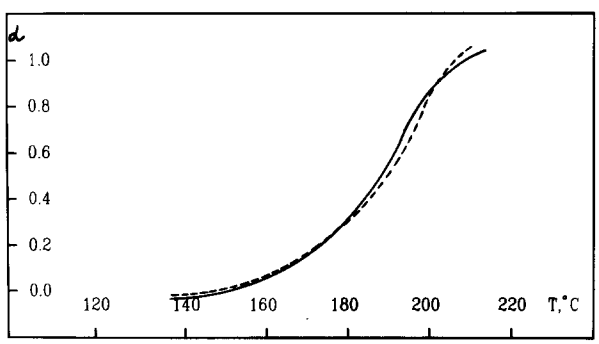

Fig. 7. Order of the reaction $n = 0.5$. Broken line, theoretical degree of conversion as the solution of kinetic equation; solid line, degree of conversion calculated from experimental data.

CONCLUSIONS

The aim of our work was to demonstrate applicability of our program. We chose calcium oxalate dehydration for this as it is one of the most extensively investigated decomposition reactions [7–10]. Table 1 contains the values of kinetic parameters reported in the literature and calculated in our experiment.

The program has been successfully used for the kinetic study of copper oxidation with barium peroxide [11] and oxygen thermodesorption in a $YBa_2Cu_3O_{6.9\pm0.1}$ superconductor [12].

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