Thermochimica Acta, 87 (1985) 345–348
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

AN EXTENSION OF THE METHOD OF ABOU-SHAABAN AND SIMONELLI FOR OBTAINING KINETIC PARAMETERS FROM TG DATA

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(Received 6 November 1984)

Numerous methods have been proposed for analyzing TG data to determine kinetic parameters. Abou-Shaaban and Simonelli have developed techniques based on several reaction cases [1]. In one of these, the reaction treated is

$$A_s \rightarrow B_s + C_g \tag{1}$$

where A_s and B_s are solids and C_g is a gaseous product. These authors derived the relationship

$$\log\left[\frac{-\mathrm{d}\left(W_{\mathrm{obs}}^{t}\right)\mathrm{d}T}{\left(W_{\mathrm{obs}}^{0}\right)-\left(W_{\mathrm{obs}}^{0}\right)/r}\right]=\log\frac{Z}{\beta}-\frac{E}{2.303RT} \tag{2}$$

where W_{obs}^{t} is the observed sample weight at time t, r is the ratio of the molecular weight of A to that of B, T is the temperature (K), β is the heating rate, Z is the frequency factor, and E is the activation energy. Thus, a plot of the left-hand side of eqn. (2) vs. $1/T$ will yield a linear plot having a slope of $-E/2.303R$. However, the rate law assumed is

$$\frac{\mathrm{d}\left(A_s^t\right)}{\mathrm{d}t}=-k\left(A_s^t\right) \tag{3}$$

where A_s^t is the weight of A present at time t. This rate law is that of a first-order process. The purpose of this communication is to provide an extension of this method to deal with cases other than the first-order case. We also present a computational scheme to carry out the process iteratively.

METHODS

Assuming the reaction to be studied is given by eqn. (1), it can be shown that

$$\alpha=\frac{W_{\mathrm{obs}}^{0}-W_{\mathrm{obs}}^{t}}{W_{\mathrm{obs}}^{0}-W_{\mathrm{obs}}^{0}/r} \tag{4}$$

where W^0_{obs} is the initial weight of the sample, W^t_{obs} is the sample weight at time t, and r is the ratio of molecular weights of A and B. We now make use of the first order rate law

$$\frac{d\alpha}{dT}=\frac{A}{\beta}(1-\alpha)e^{-E/RT} \tag{5}$$

Taking logarithms of both sides of eqn. (5) and substituting $d\alpha/dT$ obtained from eqn. (4) into the resulting equation yields

$$\ln\frac{d\alpha/dT}{1-\alpha}=\ln(A/\beta)-\frac{E}{RT} \tag{6}$$

which is equivalent to eqn. (2). Using the more general rate equation

$$\frac{d\alpha}{dT}=\frac{A}{\beta}(1-\alpha)^n e^{-E/RT} \tag{7}$$

gives

$$\ln\left[\frac{d\alpha/dT}{(1-\alpha)^n}\right]=\ln\frac{A}{\beta}-\frac{E}{RT} \tag{8}$$

It can be seen that a plot of the left-hand side of eqn. (8) vs. $1/T$ should be linear with a slope of $-E/R$ and an intercept of $\ln(A/\beta)$ for the correct value of n. This constitutes the first method of applying this extension of the method of Abou-Shaaban and Simonelli.

In order to obtain a numerical method that can be applied iteratively, a second method similar to that of Reich and Stivala was developed [2]. Considering two data sets, $(\alpha_i, T_i, (d\alpha/dT)_i)$ and $((\alpha_{i+1}, T_{i+1}, (d\alpha/dT)_{i+1})$, we obtain

$$\ln\left[\frac{(d\alpha/dT)_i}{(d\alpha/dT)_{i+1}}\left(\frac{1-\alpha_i}{1-\alpha_{i+1}}\right)^n\right]=\frac{E}{R}\left(\frac{1}{T_{i+1}}-\frac{1}{T_i}\right) \tag{9}$$

For successive data sets, a plot of the left-hand side of eqn. (9) vs. $((1/T_{i+1})-(1/T_i))$ should be linear with an intercept of zero and a slope of E/R for the correct value of n. The analysis is performed iteratively using an initial value of $n=0$ and n is incremented until the intercept closest to zero is found [2,3]. The method was implemented using a Texas Instruments TI-58 or TI-59 programmable calculator.

In order to test the method, eqn. (7) was solved numerically using a fourth-order Runge–Kutta method [4]. The $(\alpha, T, d\alpha/dT)$ data thus obtained were analyzed by both of the methods described above. In order to test the methods with actual TG data, the decomposition of $CaCO_3$ was studied using a Perkin-Elmer thermogravimetric system (Model TGS-2). Procedures used were similar to those previously described [5].

RESULTS AND DISCUSSION

The data obtained from the numerical solution of eqn. (7) using values of $n = 1/2$, $1/2$, $2/3$ and 1 are shown in Table 1. In carrying out the numerical solutions, the values of $E = 100$ kJ mol^{-1} and $A/\beta = 3 \times 10^{10}$ were used. These data were then used to test the computational methods. The results obtained using linear regression with a specific value for n (the first method) showed that analysis of these data gave linear plots for the correct n value and yielded the correct activation energy. Thus, one could test TG data using this technique employing various values of n to see which gives the most nearly linear plot.

Since it is difficult to iterate on n using the correlation coefficient as a criterion, the iterative method that searches for the n value resulting in an intercept closest to zero was developed. Table 2 shows the kinetic parameters computed using the iterative method with calculated (α, T, $(\mathrm{d}\alpha/\mathrm{d}T)$) data. The iterative method easily identifies the correct value of n and yields an E value that is virtually identical to that used in the numerical solution of the rate equation.

The results of the analysis of data for the decomposition of $CaCO_3$ are also shown in Table 2. Both the iterative method and the method using a fixed n value with linear regression gave virtually identical results. The results shown in Table 2 are those obtained using the iterative method. Kinetic parameters obtained are in reasonable agreement with those previously reported [6–8]. It is readily apparent, however, that the problem of sample-to-sample variation persists [9]. The present extension of the method of Abou-Shaaban and Simonelli allows that approach to be used for reac-

TABLE 1

Values of α and $\mathrm{d}\alpha/\mathrm{d}T$ computed from eqn. (7) using a fourth-order Runge–Kutta method [a]

T (K)	α	$\mathrm{d}\alpha/\mathrm{d}T$	α	$\mathrm{d}\alpha/\mathrm{d}T$
	$n = 1/3$		$n = 1/2$	
410	0.07056	0.0053277	0.07015	0.0052643
420	0.14676	0.010411	0.14493	0.010150
430	0.29065	0.019054	0.28338	0.018086
440	0.53996	0.031144	0.51426	0.028117
450	0.89313	0.035145	0.82452	0.031024
	$n = 2/3$		$n = 1$	
410	0.06974	0.0052024	—	—
420	0.14317	0.0099022	0.13981	0.0094420
430	0.27660	0.017216	0.26430	0.015718
440	0.49189	0.025689	0.45453	0.022006
450	0.77010	0.027793	0.68720	0.023166
460	—	—	0.88562	0.015145

[a] Computed using $E = 100$ kJ mol^{-1}, $R = 8.31441$ J mol^{-1} K^{-1}, and $A/\beta = 3 \times 10^{10}$.

TABLE 2

Results obtained using the iterative method

n (actual) [a]	n (calcd)	E (kJ mol^{-1})
Calculated (α, T, ($d\alpha/dT$)) data		
1/3	0.33	99.79
1/2	0.50	100.00
2/3	0.67	100.14
1	1.00	100.00
Run	n	E (kJ mol^{-1})
Data from decomposition of $CaCO_3$		
1	0.50	177.0
2	0.47	194.8
3	0.27	180.8
4	0.23	170.3
5	0.34	172.3
Average	0.36	179.0

[a] Value used in the numerical solutions of eqn. (7).

tions which do not follow a first-order rate law and the computational methods greatly increase the speed and accuracy of the analysis of the data.

ACKNOWLEDGMENT

The authors would like to acknowledge helpful suggestions from Dr. L. Reich concerning the initiation of this work.

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