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A METHOD FOR THE KINETIC ANALYSIS OF NONISOTHERMAL DECOMPOSITION REACTIONS OF SOLIDS

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ABSTRACT

A new method, which allows the determination of the mechanism of a decomposition reaction of solids and leads to reliable kinetic parameters, is proposed. The test of the validity of the method is performed with seven simulated TG and DTG curves.

INTRODUCTION

Nonisothermal methods for determining kinetic parameters offer interesting advantages over conventional isothermal studies [1]: only a single sample and fewer data are required and the kinetics can be calculated over an entire temperature range in a continuous manner. Also, if the sample undergoes considerable reaction when the temperature is raised to the optimal, the results obtained by an isothermal method are often questionable.

A disadvantage of the nonisothermal method, when compared with the isothermal one, is that the reaction mechanism cannot usually be determined, and, hence, the meaning of the kinetic parameters is uncertain.

On the other hand, the most widely used commercial apparatus for thermal analysis are equipped with linear temperature programmers. In these conditions the methods usually employed for kinetic analysis [2–9] lead to ambiguous results, especially if the studied reaction follows a diffusion-controlled kinetic law.

As known, the rate of a reaction of thermal decomposition of solids can be expressed by the general equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\ \mathrm{e}^{-E/\mathrm{R}T}\mathrm{f}(\alpha) \tag{1}$$

where $\mathrm{f}(\alpha)$ is a function which depends on the actual reaction mechanism.

When the temperature of the sample is increased at a constant rate,

$$\beta = \frac{\mathrm{d}T}{\mathrm{d}t}$$

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we can write

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} \exp(-E/\mathrm{R}T)\mathrm{f}(\alpha) \tag{2}$$

and, by integration,

$$\mathrm{g}(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp(-E/\mathrm{R}T)\,\mathrm{d}T \tag{3}$$

By differentiating the logarithmic form of eqn. (1) with respect to d(ln(1 − α)), we obtain

$$\frac{\mathrm{d}(\ln(\mathrm{d}\alpha/\mathrm{d}T))}{\mathrm{d}(\ln(1-\alpha))} = -\frac{E}{\mathrm{R}} \frac{\mathrm{d}(1/T)}{\mathrm{d}(\ln(1-\alpha))} + \frac{\mathrm{d}(\ln \mathrm{f}(\alpha))}{\mathrm{d}(\ln(1-\alpha))}$$

or

$$\frac{\Delta(\ln(\mathrm{d}\alpha/\mathrm{d}T))}{\Delta(\ln(1-\alpha))} = -\frac{E}{\mathrm{R}} \frac{\Delta(1/T)}{\Delta(\ln(1-\alpha))} + \frac{\Delta(\ln \mathrm{f}(\alpha))}{\Delta(\ln(1-\alpha))} \tag{4}$$

The Freeman and Carroll method [3] is based on eqn. (4), assuming

$$\mathrm{f}(\alpha) = (1-\alpha)^n \tag{5}$$

However, according to Criado et al. [10], the linear representations based on eqn. (4) lead to a straight line, even when the mechanism of the reaction cannot be represented by eqn. (5). Therefore, this method does not allow one to determine if a reaction is obeying an "*n*th order" kinetic law or a different one.

THEORY

We can write eqn. (4) in the form

$$\frac{\Delta(\ln(\mathrm{d}\alpha/\mathrm{d}T)) - \Delta(\ln \mathrm{f}(\alpha))}{\Delta(\ln(1-\alpha))} = -\frac{E}{\mathrm{R}} \frac{\Delta(1/T)}{\Delta(\ln(1-\alpha))} \tag{6}$$

and, thus, the plots of the left-hand side of eqn. (6) against $\Delta(1/T)/\Delta\ln(1-\alpha)$ should be a straight line with a slope of $-E/\mathrm{R}$, irrespective of the f(α) employed. However, we can select the f(α) that best fit the actual mechanism of the studied reaction by means of the intercept value, which, in an ideal agreement with eqn. (6), should be zero.

In order to test the validity of the above considerations, we have constructed both the TG and DTG curves corresponding to the seven mechanisms listed in Table 1, using the following kinetic parameters: $E = 125.4$ kJ mol^{-1} (30 kcal mol^{-1}), $A = 10^{13}$ s^{-1} and a heating rate of 10 K min^{-1}. The integration of the Arrhenius equation was performed by a third-order

TABLE 1

Kinetic equations used for the construction of the simulated decomposition reactions

Mechanism	$q(\alpha)$	$f(\alpha)$	Rate-controlling process
D1	α^2	$1/2\alpha$	Uni-dimensional diffusion
D2	$\alpha+(1-\alpha)\ln(1-\alpha)$	$(-\ln(1-\alpha))^{-1}$	Bi-dimensional diffusion
D3	$(1-(1-\alpha)^{1/3})^2$	$\frac{3/2(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}}$	Three-dimensional diffusion: Jander equation
D4	$1-2/3\alpha-(1-\alpha)^{2/3}$	$(3/2(1-\alpha)^{-1/3})^{-1}$	Three-dimensional diffusion: Ginstling–Brounshtein equation
F1	$-\ln(1-\alpha)$	$(1-\alpha)$	Random nucleation
R2	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	Phase-boundary reaction (cylindrical symmetry)
R3	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	Phase-boundary reaction (spherical symmetry)

rational approximation, developed by Senung and Yang [11], with an accuracy better than $10^{-2}\%$:

$$\int_0^T \exp(-E/RT)\,dT = \frac{E}{R}\frac{e^{-x}}{x}\frac{x^2+10x+18}{x^3+12x^2+36x+24} \tag{7}$$

For each of these seven simulated decompositions, we have performed the kinetic analysis using eqn. (6) and the seven $f(\alpha)$ proposed. The results are presented in Tables 2–8; r is the correlation coefficient, i the intercept and m the slope of the obtained straight lines.

As can easily be seen, in all cases the correlation coefficient, r, is very near to unity, in accordance with the results of Criado et al. [10]. Nevertheless, only when the analysis was performed with the appropriate $f(\alpha)$, the straight line intercepts the origin. Therefore, the intercept value close to zero can be used to select the best $f(\alpha)$. In addition, the calculated gradients show

TABLE 2

Analysis of the data corresponding to a reaction with $f(\alpha)=1/2\alpha$ (mechanism D1)

$f(\alpha)$ employed	r	i	m
D1	−0.99999	−0.0036	−15066.5
D2	−0.99997	−0.427	−15171.5
D3	−0.99998	−0.935	−15159.6
D4	−0.99998	−0.602	−15159.6
F1	−0.99995	−1.0	−7137.2
R2	−0.99995	−0.5	−7137.2
R3	−0.99995	−0.667	−7137.2

TABLE 3

Analysis of the data corresponding to a reaction with $f(\alpha) = (-\ln(1-\alpha))^{-1}$ (mechanism D2)

f(α) employed	r	i	m
D1	−0.99997	0.413	−14985.8
D2	−0.99999	−0.0004	−15090.9
D3	−0.99998	−0.51	−15878.8
D4	−0.99998	−0.177	−15078.8
F1	−0.99991	−0.695	−7128.1
R2	−0.99991	−0.195	−7128.1
R3	−0.99991	−0.362	−7128.1

TABLE 4

Analysis of the data corresponding to a reaction with $f(\alpha) = 3/2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$ (mechanism D3)

f(α) employed	r	i	m
D1	−0.99996	0.893	−14922.4
D2	−0.99999	0.514	−15101.8
D3	−0.99999	−0.0005	−15080.6
D4	−0.99999	0.333	−15080.6
F1	−0.99998	−0.329	−7176.2
R2	−0.99998	0.171	−7176.2
R3	−0.99998	0.04	−7176.2

TABLE 5

Analysis of the data corresponding to a reaction with $f(\alpha) = (3/2(1-\alpha)^{-1/3} - 1)^{-1}$ (mechanism D4)

f(α) employed	r	i	m
D1	−0.99988	0.537	−14763.8
D2	−0.99999	0.185	−15134.7
D3	−0.99999	−0.333	−15089.6
D4	−0.99999	0.0007	−15089.6
F1	−0.99997	−0.579	−7098.4
R2	−0.99997	−0.08	−7098.4
R3	−0.99997	−0.246	−7098.4

a very good agreement with the postulated value (for $E = 125.4$ kJ mol^{-1}, $E/\mathrm{R} = 15083$ K).

Once the mechanism was established, the pre-exponential factor can be calculated by applying the method of Achar et al. [9], based on the

TABLE 6

Analysis of the data corresponding to a reaction with $f(\alpha) = 1 - \alpha$ (mechanism F1)

$f(\alpha)$ employed	r	i	m
D1	−0.99999	1.389	−30681.4
D2	−0.99999	0.989	−30922.1
D3	−0.99999	0.478	−30894.4
D4	−0.99999	0.811	−30894.4
F1	−0.99997	−0.009	−15004.6
R2	−0.99997	0.489	−15004.6
R3	−0.99997	0.323	−15004.6

TABLE 7

Analysis of the data corresponding to a reaction with $f(\alpha) = 2(1-\alpha)^{1/2}$ (mechanism R2)

$f(\alpha)$ employed	r	i	m
D1	−0.99998	0.676	−30774.2
D2	−0.99999	0.273	−31062.3
D3	−0.99999	−0.238	−31029.2
D4	−0.99999	0.095	−31029.2
F1	−0.99999	−0.5	−15102.8
R2	−0.99999	−0.0001	−15102.8
R3	−0.99999	−0.167	−15102.8

TABLE 8

Analysis of the data corresponding to a reaction with $f(\alpha) = 3(1-\alpha)^{2/3}$ (mechanism R3)

$f(\alpha)$ employed	r	i	m
D1	−0.99999	0.905	−30618.9
D2	−0.99999	0.49	−30843.3
D3	−0.99999	−0.019	−30817.8
D4	−0.99999	0.314	−30817.8
F1	−0.99996	−0.349	−14950.9
R2	−0.99996	0.151	−14950.9
R3	−0.99996	−0.005	−14950.9

expression

$$\ln\left(\frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)}\right) = \ln\frac{A}{\beta} - \frac{E}{RT} \tag{8}$$

and employing the $f(\alpha)$ previously established. Table 9 summarizes the

TABLE 9

Results of the kinetic analysis of the seven simulated processes: (1) calculated by the proposed method; (2) calculated by Achar's method (E/R in K, A in s^{-1})

Mechanism	E/R (1)	E/R (2)	$A/10^{13}$
D1	15066.5	15087.3	1.01
D2	15090.9	15088.6	1.01
D3	15080.6	15084.8	1.0
D4	15089.6	15083.3	1.0
F1	15004.6	15096.2	1.03
R2	15102.8	15102.6	1.05
R3	14950.9	15080.2	0.994

results obtained from our method, and by application of Achar's method. The values for A were also very close to the postulated value of 10^{13} s^{-1}.

CONCLUSION

The proposed method allows the determination of the mechanism of a decomposition reaction for solids, and leads to reliable kinetic parameters, using the TG and DTG results obtained in a single run with linear progression of temperature.

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