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Note

EVALUATION OF THE NON-ISOTHERMAL KINETIC PARAMETERS OF HETEROGENEOUS SOLID–GAS DECOMPOSITIONS WITH THE HELP OF AN INTEGRAL METHOD

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The integral methods used for non-isothermal kinetic analysis are widespread and well-known [1,2]. They are generally based on approximate solutions of the temperature integral. In this paper, the results of an attempt to avoid the approximate evaluation of the temperature integral are presented. To develop this integral method, we shall begin with the general non-isothermal rate equation

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

where all the symbols have their usual meanings. For generality, the temperature dependence of the pre-exponential factor will be considered as follows

$$A = A_r T^r \tag{2}$$

As far as the conversion function is concerned, its general form is [3]

$$\mathrm{f}(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \tag{3}$$

Equation (1), taking into account relationship (2), becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A_r}{\beta} T^r\, \mathrm{e}^{-E/RT} \mathrm{d}T \tag{4}$$

or

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha) T^{r+2}} = \frac{A_r}{\beta} \frac{\mathrm{e}^{-E/RT}}{T^2} \mathrm{d}T \tag{5}$$

The integral form of eqn. (5) is

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha) T^{r+2}} = \frac{A_r}{\beta} \int_0^{T} \frac{\mathrm{e}^{-E/RT}}{T^2} \mathrm{d}T \tag{6}$$

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The right-hand side integral can be solved exactly, with the following results

$$\int_0^T \frac{e^{-E/RT}}{T^2} dT = \frac{R}{E} e^{-E/RT} \tag{7}$$

As far as the left-hand side of eqn. (6) is concerned, because of the lack of information on the analytical form of the dependence of $T(\alpha)$, a graphical or numerical integration should be performed.

Taking into account eqn. (7), eqn. (6) becomes

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)T^{r+2}} = \frac{A_r R}{\beta E} e^{-E/RT} \tag{8}$$

or taking logarithms

$$\log \int_0^\alpha \frac{d\alpha}{f(\alpha)T^{r+2}} = \log \frac{A_r R}{\beta E} - \frac{E}{2.303RT} \tag{9}$$

if $m = p = 0$, and thus $f(\alpha) = (1-\alpha)^n$, for the correct value of n the plot

$$\left[\log \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n T^{r+2}}, \frac{1}{T}\right]$$

should be a straight line whose slope and intercept give the activation energy and pre-exponential factor values, respectively.

In our practical calculations the integral from the left-hand side of eqn. (9) was evaluated using the trapezoidal method for non-equally distanced points [4]. According to this method, if

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n T^{r+2}} = I_{\alpha_i} \tag{10}$$

then

$$I_{\alpha_{i+1}} = I_{\alpha_i} + (\alpha_{i+1} - \alpha_i)\left[\frac{g(\alpha_{i+1}) + g(\alpha_i)}{2}\right] \tag{11}$$

where

$$\frac{1}{(1-\alpha)^n T^{r+2}} = g(\alpha)$$

The condition $I_{\alpha=0} = 0$ should also be taken into account.

Formally, our integral method is quite similar to that given by Coats and Redfern [5]. However, our method is not based on approximate calculations of the temperature integral. One can object that a graphical or numerical integration could also be performed to evaluate the temperature integral, and that our method only shifts the graphical or numerical integration to the first member of eqn. (9). Actually, this shift increases the accuracy of the calculations. Indeed, in the temperature integral, temperature appears in the form $e^{-E/RT}$ while in the first member of eqn. (9), the temperature function is T^{r+2}.

To check the validity of the method, it was applied to the dehydration of calcium oxalate monohydrate. To evaluate the activation energy, E, and the pre-exponential factor, A_r, the least-squares method was used [6]. To appreciate the degree of linearity of the plots

$$\left[\log \int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^r T^{r+2}}, \frac{1}{T}\right]$$

the correlation coefficient, r_{xy}, was calculated [6]. The results are given in Table 1.

An inspection of these results shows that the best results in fair agreement with those reported in the literature correspond to $n = 1$ and $r = 0$ [2,5]. For $r = 2$ and $r = 3$, a small decrease in the activation energy and a more drastic decrease in the pre-exponential coefficient are recorded. A small decrease in the correlation coefficient can also be noticed.

The value $r = 0$, which is the most probable, shows the advantages of the proposed method, the left-hand side of eqn. (9), which contains in the denominator T^2, being less sensitive to the experimental errors in temperature measurements than the true temperature integral, and thus being more suitable for graphical or numerical integration.

CONCLUSIONS

(1) An integral method for the evaluation of the non-isothermal kinetic parameters which avoids the approximate calculation of the temperature integral was produced.

(2) The values of the kinetic parameters of the dehydration of calcium oxalate monohydrate, calculated with this integral method, are in fairly good agreement with those reported in the literature.

TABLE 1

Kinetic parameters for the dehydration of calcium oxalate

n	r	E (kcal mol^{-1})	A_r	r_{xy}
1	0	23.900	1.2×10^8 s^{-1}	−0.995
1	1	23.000	9.0×10^4 s^{-1} K^{-1}	−0.993
1	2	22.000	7.7×10^1 s^{-1} K^{-2}	−0.992

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