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Note

A NEW METHOD FOR THE EVALUATION OF NON-ISOTHERMAL KINETIC PARAMETERS USING INTEGRATION OVER SMALL TEMPERATURE INTERVALS AND SEVERAL HEATING RATES

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In the fundamental differential equation of non-isothermal kinetics [1–3]

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

where for the sake of generality [4]

$$\mathrm{f}(\alpha)=(1-\alpha)^n\alpha^m[-\ln(1-\alpha)]^p \tag{2}$$

we shall use the following heating rates: β_1, $\beta_2,\ldots\beta_l,\ldots\beta_v$. Taking into account that β_l $(l=1, 2,\ldots v)$ could not be strictly constant over the temperature interval where the reaction occurs, one has to consider the heating rates β_{1ij}, $\beta_{2ij},\ldots\beta_{lij},\ldots\beta_{vij}$ where β_{lij} $(l=1, 2,\ldots v)$ corresponds to the interval $\alpha\in[\alpha_i, \alpha_j]$, its value being slightly different from the programmed one. In the following, the isoconversion temperature for $\alpha=\alpha_i$, T_{1i}, $T_{2i},\ldots T_{li},\ldots T_{vi}$ corresponding to different heating rates will be used.

EVALUATION OF THE ACTIVATION ENERGY

Let us consider the heating rates β_{lik} $(l=1, 2,\ldots v)$ for the temperatures T_{li} and T_{lk} corresponding to the values α_i and α_k of the conversion degree, respectively.

From eqn. (1) through variable separation and integration, one obtains

$$\int_{\alpha_i}^{\alpha_k}\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)}=\frac{A_r}{\beta_{lik}}\int_{T_{li}}^{T_{lk}}T^r\,\mathrm{e}^{-E/RT}\mathrm{d}T \tag{3}$$

for $l=1, 2,\ldots v$.

If $\mathrm{f}(\alpha)$ keeps the same form for various heating rates, it follows from eqn. (3) that

$$1/\beta_{lik}\int_{T_{li}}^{T_{lk}}T^r\,\mathrm{e}^{-E/RT}\mathrm{d}T=1/\beta_{l+1ik}\int_{T_{l+1i}}^{T_{l+1k}}T^r\,\mathrm{e}^{-E/RT}\mathrm{d}T \tag{4}$$

for $l=1, 2,\ldots v-1$.

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From relationship (4), one can evaluate the activation energies $E_{12}(l=1)$, $E_{23}(l=2), \ldots E_{v-1,v}(l=v-1)$. If E_{ll+1} keeps a constant value for all the l values, then the conversion function, f(α), does not change its form.

ON THE FORM OF THE CONVERSION FUNCTION, f(α)

Let us consider a third value of the conversion degree, $\alpha_j \in (\alpha_i, \alpha_k)$, preferably in the middle of the interval, i.e.

$$\alpha_j = \frac{\alpha_i + \alpha_k}{2} \tag{5}$$

For a certain heating rate, l, one can write the following two relationships

$$\int_{\alpha_i}^{\alpha_j} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A_r}{\beta_{lij}} \int_{T_{li}}^{T_{lj}} T^r \,\mathrm{e}^{-E/RT} \,\mathrm{d}T \tag{6}$$

$$\int_{\alpha_j}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A_r}{\beta_{ljk}} \int_{T_{lj}}^{T_{lk}} T^r \,\mathrm{e}^{-E/RT} \,\mathrm{d}T \tag{7}$$

From relationships (6) and (7), one obtains

$$\frac{\displaystyle\int_{\alpha_j}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)}}{\displaystyle\int_{\alpha_j}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)}} = \frac{\beta_{lij}}{\beta_{ljk}} \frac{\displaystyle\int_{T_{lj}}^{T_{lk}} T^r \,\mathrm{e}^{E/RT} \,\mathrm{d}T}{\displaystyle\int_{T_{li}}^{T_{lj}} T^r \,\mathrm{e}^{-E/RT} \,\mathrm{d}T} \tag{8}$$

This result allows the most suitable form of the conversion function, f(α), to be chosen which fulfills relationship (8).

EVALUATION OF THE FACTOR A_r

From relationship (3) it turns out that

$$A_r = \beta_{lik} \frac{\displaystyle\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)}}{\displaystyle\int_{T_{li}}^{T_{lk}} T^r \,\mathrm{e}^{-E/RT} \,\mathrm{d}T} \tag{9}$$

for $l = 1, 2, \ldots v$.

PARTICULAR VARIATION OF THE METHOD FOR $r=0$; $A=ct$; $\mathrm{f}(\alpha)=(1-\alpha)^n$ WITH TWO HEATING RATES (β_1 AND β_2)

From mathematical analysis [5,6]

$$\int_a^b \mathrm{f}(x) \,\mathrm{d}x = (b-a)\,\mathrm{f}(\xi) \tag{10}$$

where $\xi \in (a, b)$. When $f(x) = mx + n$ (linear function), then $\xi = (a + b)/2$. For $T_{lk} - T_{li} \leqslant 15$–$20$ K, $e^{-E/RT}$ can be approximated as linear, taking into account the theorem [10], one obtains

$$\int_{T_{li}}^{T_{lk}} e^{-E/RT} \mathrm{d}T \approx (T_{lk} - T_{li})\, e^{-E/RT_{lik}} \tag{11}$$

where

$$T_{lik} = \frac{T_{li} + T_{lk}}{2} \tag{12}$$

By help of the same theorem (10), the conversion integral can be approximated in the following way

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{(1 - \alpha)^n} \approx (\alpha_k - \alpha_i) \frac{1}{(1 - \alpha_{ik})^n} \tag{13}$$

where

$$\alpha_{ik} = \frac{\alpha_i + \alpha_k}{2} \tag{14}$$

The particular form of relationship (4) for the case considered is

$$\frac{1}{\beta_{1ik}} \int_{T_{1i}}^{T_{1k}} e^{-E/RT} \mathrm{d}T = \frac{1}{\beta_{2ik}} \int_{T_{2i}}^{T_{2k}} e^{-E/RT} \mathrm{d}T \tag{15}$$

Using relationship (11) it turns out that

$$\frac{T_{1k} - T_{1i}}{\beta_{1ik}} e^{-E/RT_{1ik}} = \frac{T_{2k} - T_{2i}}{\beta_{2ik}} e^{-E/RT_{2ik}} \tag{16}$$

This result allows the activation energy to be obtained.

$$E = R \frac{T_{1ik} T_{2ik}}{T_{2ik} - T_{1ik}} \ln \frac{\beta_{2ik}(T_{1k} - T_{1i})}{\beta_{1ik}(T_{2k} - T_{2i})} \tag{17}$$

To determine the n value using relationship (8) and the approximations (11) and (13) one can write

$$\frac{(\alpha_k - \alpha_j)/(1 - \alpha_{jk})^n}{(\alpha_j - \alpha_i)/(1 - \alpha_{ij})^n} = \frac{\beta_{lij}}{\beta_{ljk}} \frac{(T_{lk} - T_{lj})}{(T_{lj} - T_{li})} \frac{e^{-E/RT_{ljk}}}{e^{-E/RT_{lij}}} \tag{18}$$

From the logarithmic form of relationship (18), taking into account relationship (5), one obtains

$$n_1 \approx \frac{1}{\ln[(1 - \alpha_{ij})/(1 - \alpha_{jk})]} \left[\ln \frac{\beta_{1ij}(T_{1k} - T_{1j})}{\beta_{1jk}(T_{1j} - T_{1i})} + \frac{E}{R} \left(\frac{T_{1jk} - T_{1ij}}{T_{1jk} T_{1ij}} \right) \right] \tag{19}$$

Similarly, for β_2 another value n_2 will be obtained. Thus

$$n = \frac{n_1 + n_2}{2} \tag{20}$$

Finally, the pre-exponential factor, A, can be evaluated from relationships (9), (11) and (13)

$$A_l \approx \beta_{lik} \frac{(\alpha_k - \alpha_i)[1/(1 - \alpha_{ik})^n]}{(T_{lk} - T_{li})\, \mathrm{e}^{-E/RT_{lik}}} \tag{21}$$

for $l = 1, 2$, where

$$\log A = \frac{\log A_1 + \log A_2}{2} \tag{22}$$

APPLICATIONS

The method was applied to a known test reaction, the dehydration of calcium oxalate, for two heating rates: $\beta_1 = 1$ and $\beta_2 = 5$ K min^{-1}. The non-isothermal kinetic parameters have been calculated for several groups of values, α_i, α_k. The results are presented in Table 1. A summary analysis of these results shows that only for $0.42 \leqslant \alpha \leqslant 0.67$ do the values of the kinetic parameters of calcium oxalate dehydration correspond to those reported in the literature [7–9]. Thus, our method using small temperature intervals shows changes in the values of the kinetic parameters from the initial period characterized by higher values of the activation energy to the normal one for which the kinetic parameter values are reported in the literature and maybe to the final decay period [10]. This sensitivity to the periods of heterogeneous solid–gas decomposition is perhaps a major advantage of our method.

TABLE 1
Non-isothermal kinetic parameters for different α_i, α_j, α_k

l	β_{lik} (K min^{-1})	T_{li} (K)	T_{lj} (K)	T_{lk} (K)
$\alpha_i = 0.0417$; $\alpha_j = 0.1042$; $\alpha_k = 0.1667$; $E = 33.9$ kcal mol^{-1}; $n = 1.57$; $A = 2.7 \times 10^{14}$ s^{-1}				
1	1.021	406	412.4	416.5
2	5.132	416	426	431.5
$\alpha_i = 0.1667$; $\alpha_j = 0.2917$; $\alpha_k = 0.4167$; $E = 25.9$ kcal mol^{-1}; $n = 1.34$; $A = 1.8 \times 10^{10}$ s^{-1}				
1	1.024	416.5	422.5	427
2	4.950	431.5	439.5	446.5
$\alpha_i = 0.4167$; $\alpha_j = 0.5417$; $\alpha_k = 0.6667$; $E = 22.6$ kcal mol^{-1}; $n = 1.01$; $A = 4.34 \times 10^{8}$ s^{-1}				
1	0.86	427	430	433
2	4.75	446.5	451	456
$\alpha_i = 0.6667$; $\alpha_j = 0.7917$; $\alpha_k = 0.9167$; $E = 18.8$ kcal mol^{-1}; $n = 0.74$; $A = 6.27 \times 10^{6}$ s^{-1}				
1	1.1	433	436	439.7
2	5.26	456	460.2	466

CONCLUSIONS

(1) A method for the evaluation of non-isothermal kinetic parameters has been developed.

(2) The method exhibits sensitivity to the main periods of the heterogeneous solid–gas decompositions.

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