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Note

INTEGRAL METHOD OF KINETIC DATA EVALUATION

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A kinetic equation has been derived by integration of the non-isothermal rate equation over small temperature intervals. The values of the kinetic parameters for the dehydration of calcium oxalate obtained by use of this equation are in satisfactory agreement with those reported in the literature.

Much work has been dedicated to the integral methods used to evaluate the non-isothermal kinetic parameters [1–3]. One of the starting relationships whose treatment leads to integral working formulae is:

$$\int_{\alpha_1}^{\alpha_2} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \int_{T_1}^{T_2} \frac{A}{a} \mathrm{e}^{-E/RT} \mathrm{d}T \tag{1}$$

where α is conversion degree, $\mathrm{f}(\alpha)$ is the conversion function, T is the temperature (K), A is the pre-exponential factor, E is the activation energy, and a is the heating rate. The general form of the conversion function is [4]

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

As far as the pre-exponential factor is concerned, its general form is:

$$A = A_r T^r \tag{3}$$

where A_r is a constant and the exponent r takes integer and half integer, positive and negative values [5].

As first approximations for the conversion function and pre-exponential factor, common cases corresponding to $m = p = 0$ in eqn. (2) and $r = 0$ in eqn. (3) will be considered, i.e.

$$\mathrm{f}(\alpha) = (1-\alpha)^n \tag{4}$$

and

$$A = A_0 \tag{5}$$

Relationship (1) for conditions (4) and (5) takes the form

$$\int_{\alpha_1}^{\alpha_2} \frac{\mathrm{d}\alpha}{(1-\alpha)^n} = \frac{A}{a} \int_{T_1}^{T_2} \mathrm{e}^{-E/RT} \mathrm{d}T \tag{6}$$

In the following, linear heating programs ($a = \mathrm{d}T/\mathrm{d}t = $ const) will be considered.

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To solve approximately the two integrals from relationship (6) the theorem of the mean from the integral calculus, according to which [6]

$$\int_a^b f(x)dx = (b-a)f(\xi) \qquad \xi \in [a,b] \tag{7}$$

will be used. If $f(x)$ is a linear function of the variable x, i.e.

$$f(x) = ax + b \tag{8}$$

the following is easily obtainable

$$\xi = \frac{a+b}{2} \tag{9}$$

For small temperature and corresponding conversion degree intervals the functions $\exp(-E/RT)$ and $1/(1-\alpha)^n$ can be considered as linear. In such condition taking into account eqn. (7) and performing the integration in eqn. (6) one gets

$$\frac{(\alpha_2 - \alpha_1)}{(1-\alpha_{12})^n} = \frac{A}{a}(T_2 - T_1)e^{-E/RT_{12}} \tag{10}$$

where

$$\alpha_{12} = \frac{\alpha_1 + \alpha_2}{2} \tag{11}$$

and

$$T_{12} = \frac{T_1 + T_2}{2} \tag{12}$$

Considering three variants of eqn. (10) for the temperatures T_1, T_2, T_3, T_4, T_5 and T_6 so that $T_2 - T_1 = T_4 - T_3 = T_6 - T_5 = T_3 - T_2 = T_5 - T_4 = \Delta T$ one gets

$$\begin{aligned}
\log A + n\log(1-\alpha_{12}) - \frac{E}{2.303RT_{12}} &= \log\frac{\alpha_2 - \alpha_1}{T_2 - T_1}a \\
\log A + n\log(1-\alpha_{34}) - \frac{E}{2.303RT_{34}} &= \log\frac{\alpha_4 - \alpha_3}{T_4 - T_3}a \\
\log A + n\log(1-\alpha_{56}) - \frac{E}{2.303RT_{56}} &= \log\frac{\alpha_6 - \alpha_5}{T_6 - T_5}a
\end{aligned} \tag{13}$$

where $T_{jj+1} = (T_j + T_{j+1})/2$ and $\alpha_{jj+1} = (\alpha_j + \alpha_{j+1})/2$. By solving the system of linear equations (13) the unknown values of the kinetic parameters A, E and n are obtained.

The temperature interval ΔT should be chosen in such a way that the corresponding $\Delta\alpha$ difference should be insensitive to the errors of the α values.

The described method was checked for the dehydration of calcium oxalate according to the following reaction

$$CaC_2O_4 \cdot H_2O(s) \rightarrow CaC_2O_{4(s)} + H_2O_{(g)}$$

By solving system (13) with the following experimental data

T	478	488	498	508	518	528
α	0.1252	0.2110	0.3333	0.4898	0.6871	0.8408

the following results are obtained: $n = 0.98$; $E = 22.7$ kcal mol^{-1}; $A = 3.45 \times 10^7$ s, which are in satisfactory agreement with those reported in the literature [7].

Considering the conversion function (2) and the pre-exponential factor (3) the method can be generalized as follows

$$\int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{(1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p} = \frac{A_r}{a} \int_{T_1}^{T_2} T^r \, e^{-E/RT} dT \tag{14}$$

Using the theorem of the mean the following is obtained

$$\frac{\alpha_2 - \alpha_1}{(1-\alpha_{12})^n \alpha_{12}^m [-\ln(1-\alpha_{12})]^p} = \frac{A_r}{a}(T_2 - T_1) T_{12}^r \, e^{-E/RT_{12}} \tag{15}$$

whose logarithmic variant is

$$\log A_r + r \log T_{12} + n \log(1-\alpha_{12}) + m \log \alpha_{12} + p \log[-\ln(1-\alpha_{12})] - \frac{E}{2.303RT_{12}} = \log \frac{\alpha_2 - \alpha_1}{T_2 - T_1} a \tag{16}$$

To get the six values of the kinetic parameters n, m, p, r, A and E six variants of eqn. (16) from twelve pairs of (α, T) values have to be considered.

CONCLUSIONS

An integral method to evaluate the non-isothermal kinetic parameters has been given. The integral kinetic equation was established by considering small temperature intervals.

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