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Short Communication

INTEGRAL DEPENDENT ON PARAMETER E IN CLASSICAL NON-ISOTHERMAL KINETICS WITH LINEAR HEATING RATE

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A simple procedure to obtain the derivative of the temperature integral with respect to the activation energy is presented.

The integral kinetic Equation of non-isothermal kinetics [1–3]:

$$\int_0^{\alpha} \frac{d(\alpha)}{f(\alpha)} = \frac{A}{\beta} \int_0^{T} e^{-\frac{E}{RT}} \mathrm{d}T \tag{1}$$

with the usual meanings of the notations and with A = const., E = const. and $f(\alpha)$ keeping its form unchanged for $0<\alpha<1$, is often used to evaluate the kinetic parameters from a set of experimental data $\alpha_{i,\mathrm{exp}}$ and $T_{i,\mathrm{exp}}$ ($i = 1, 2, \ldots, N$), N being the total number of data points. Taking into account

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = F(\alpha) \tag{2}$$

where $F(\alpha)$ is the conversion integral, and introducing the notation:

$$I(T, E) = \int_0^{T} e^{-\frac{E}{RT}} \mathrm{d}T \tag{3}$$

the following differences for the least squares method calculation can be considered [4–6]:

$$S_1 = \sum_{i=1}^{N} \left(F(\alpha_{i,\mathrm{exp}}) - \frac{A}{\beta} I(T_{i,\mathrm{exp}}, E)\right)^2 \tag{4}$$

$$S_2 = \sum_{i=1}^{N} \left(\alpha_{i,\mathrm{exp}} - G\left(\frac{A}{\beta} I(T_{i,\mathrm{exp}}, E)\right)\right)^2 \tag{5}$$

where $G\left(\frac{A}{\beta} I(T_{i,\mathrm{exp}}, E)\right)$ is the solution of Eq. (1) with respect to α. It is known that the kinetic parameters can be evaluated from the conditions of the minimum of sum S_1 or S_2. In order to perform the minimization, we need the partial derivatives $\frac{\partial S_1}{\partial E}$ and $\frac{\partial S_2}{\partial E}$. Their calculation requires the derivatives $\frac{\mathrm{d}I(T, E)}{\mathrm{d}E}$.

Integrals such as $I(T, E)$ will be called integrals dependent on one parameter (in particular E). For such integrals, the following theorem is valid [7–9]: if a function $g(x, \lambda)$, together with its partial derivative $g(x, \lambda)$, is defined and continuous for

$$a \leqslant x \leqslant b$$

$$\lambda_1 \leqslant \lambda \leqslant \lambda_2$$

then the function

$$H(\lambda) = \int_a^b g(x, \lambda)\,\mathrm{d}x$$

has a continuous derivative with respect to λ given by

$$H'(\lambda) = \frac{d}{\mathrm{d}\lambda} \int_a^b g(x, \lambda)\,\mathrm{d}x \tag{6}$$

or

$$H'(\lambda) = \int_a^b g'(x, \lambda)\,\mathrm{d}x \tag{6'}$$

As the function $e^{-\frac{E}{RT}}$ fulfils the requirements of the above-mentioned theorem:

$$\frac{\mathrm{d}I(T, E)}{\mathrm{d}E} = \int_0^T \frac{\partial e^{-\frac{E}{RT}}}{\partial E}\,\mathrm{d}T \tag{7}$$

or:

$$\frac{\mathrm{d}I(T, E)}{\mathrm{d}E} = -\int_0^T \frac{e^{-\frac{E}{RT}}}{RT}\,\mathrm{d}T \tag{8}$$

Through integration by parts, the right-hand side of relationship (8) becomes

$$-\int_0^T \frac{e^{-\frac{E}{RT}}}{RT}\,\mathrm{d}T = -\frac{1}{R}\left(\frac{RT}{E}e^{-\frac{E}{RT}}\Big|_0^T - \int_0^T \frac{R}{E}e^{-\frac{E}{RT}}\,\mathrm{d}T\right) \tag{9}$$

Introducing this result in (8), we obtain:

$$\frac{\mathrm{d}I(T,E)}{\mathrm{d}E} = \frac{1}{E}\left(\int_0^T e^{-\frac{E}{RT}}\,\mathrm{d}T - Te^{-\frac{E}{RT}}\right) \tag{10}$$

In some cases [1, 2, 10–12], the integral $\int_0^T e^{-\frac{E}{RT}}\,\mathrm{d}T$ is approximated as follows:

$$\int_0^T e^{-\frac{E}{RT}}\,\mathrm{d}T = \frac{RT^2}{E}e^{-\frac{E}{RT}}Q(T,E) \tag{11}$$

where $Q(T, E)$ is a function which changes slowly with temperature. A rough approximation of $Q(T, E)$ is unity.

Introducing (11) in (10), we obtain:

$$\frac{\mathrm{d}I(T,E)}{\mathrm{d}E} = \frac{T}{E}e^{-\frac{E}{RT}}\left(\frac{RT}{E}Q(T,E) - 1\right) \tag{12}$$

a result which can be used in least squares calculations.

Conclusions

In order to facilitate the use of the least squares method to evaluate non-isothermal kinetic parameters, a simple calculation of the derivative of the temperature integral with respect to the activation energy was performed.

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