Short Communications

MATHEMATICAL ANALYSIS OF THERMOKINETIC CURVES FOR AUTOCATALYTICALLY DECOMPOSING SUBSTANCES

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The mathematical analysis of thermokinetic curves described by the differential equation $\frac{d\alpha}{dt} = K\alpha(1 - \alpha)$ has been performed, and an integral expression for this equation was obtained.

In the practice of isothermal studies of the kinetics of solid-phase transformations, substances occur which decompose according to the well-known law of autocatalysis expressed by the Prout—Tomkins equation [1, 2]

$$d\alpha/dt = K\alpha(1 - \alpha) \tag{1}$$

where α is the degree of decomposition or transformation. The kinetic curve of this type of transformation is symmetrical with respect to $\alpha = 0.5$, where maximum rate of transformation is observed.

The mathematical and kinetic analysis of the thermokinetic decomposition curves of such substances under the conditions of controlled heating [3, 4, 5] is certainly of interest. Accepting the Arrhenius model for the temperature dependence of the rate constant, Eq. (1) can be written in the following form:

$$d\alpha/dt = A \exp\left(-E_a/RT\right)\alpha(1 - \alpha) \tag{2}$$

Let us determine the integral form of Eq. (2). According to the solution of the temperature integral proposed by us, integration will lead to

$$\ln\frac{\alpha}{1 - \alpha} = \frac{A}{q}\left(\frac{RT^2}{E + 2RT}\right)\exp\left(\frac{-E_a}{RT}\right) + C \tag{3}$$

In order to determine the integration constant C, the value of A is required. According to the concept presented in our earlier paper [6], A is expressed in the following way:

$$A = \frac{E_a \cdot q}{RT_m^2(2\alpha - 1)}\exp\frac{E_a}{RT_m} \tag{4}$$

Hence Eq. (3) can be written as follows:

$$\ln \frac{\alpha}{1 - \alpha} = \frac{\left(\dfrac{T}{T_{\mathrm{m}}}\right)^2 E_{\mathrm{a}}}{(2\alpha_{\mathrm{m}} - 1)(E_{\mathrm{a}} + 2RT)} \exp\left(\frac{E_{\mathrm{a}}\Theta}{RT_{\mathrm{m}}T}\right) + C \tag{5}$$

where $\theta = T - T_{\mathrm{m}}$. The integration constant C is found by putting $T = T_{\mathrm{m}}$:

$$C = \ln \frac{\alpha_{\mathrm{m}}}{1 - \alpha_{\mathrm{m}}} - \frac{E_{\mathrm{a}}}{(2\alpha_{\mathrm{m}} - 1)(E_{\mathrm{a}} + 2RT_{\mathrm{m}})}. \tag{6}$$

After substitution of C into Eq. (5), we finally obtain the full solution of the initial differential equation (2) in the following form:

$$\ln \frac{\alpha(1 - \alpha_{\mathrm{m}})}{\alpha_{\mathrm{m}}(1 - \alpha)} = \frac{\left(\dfrac{T}{T_{\mathrm{m}}}\right)^2 E_{\mathrm{a}} \exp\left(\dfrac{E_{\mathrm{a}}\theta}{RT_{\mathrm{m}}T}\right)}{(2\alpha_{\mathrm{m}} - 1)(E_{\mathrm{a}} + 2RT)} - \frac{E_{\mathrm{a}}}{(2\alpha_{\mathrm{m}} - 1)(E_{\mathrm{a}} + 2RT_{\mathrm{m}})} \tag{7}$$

The use of the integral equation (7) for the practical determination of the activation energy E_{a} without the differential kinetic curve is very inconvenient, owing to the difficulty in establishing the values α_{m} and T_{m}. For this reason, it is proposed in the literature to determine the activation energy E_{a} from the differential equations [4, 5]:

$$\ln \left(\frac{d\alpha/dt}{\alpha(1 - \alpha)}\right) = \ln A - \frac{E_{\mathrm{a}}}{RT} \tag{8}$$

by plotting the relationship $\ln \left(\dfrac{d\alpha/dt}{\alpha(1 - \alpha)}\right)$ $vs.$ $1/T$. However, this computation may be simplified somewhat for the range $\alpha = 0.3$ to 0.7, since in this range $\alpha(1 - \alpha) \approx 0.23$. Then

$$\ln \frac{d\alpha}{dt} = \frac{-E_{\mathrm{a}}}{RT} + \text{const.} \tag{9}$$

or, if changing to the corresponding heights h_{i} on the kinetic curves of DTG or DSC, we obtain:

$$\ln h_{\mathrm{i}} = -\frac{E_{\mathrm{a}}}{RT} + \text{const.} \tag{10}$$

Let us analyze the kinetic curve with the aid of the well-known kinetic equation:

$$\frac{d\alpha}{dt} = A_{\mathrm{n}} \exp\left(-\frac{E_{\mathrm{n}}}{RT}\right)(1 - \alpha)^{\mathrm{n}} \tag{11}$$

where n is the kinetic exponent, sometimes termed formal order of the decomposition. In the point of maximum rate of transformation $\left(\dfrac{d^2\alpha}{dt^2}\right)_{\mathrm{m}}$ is zero on the

DTG or DSC curves. After the necessary transformations, one obtains for the case of linear heating

$$E_a = \frac{RT_m^2(2\alpha_m - 1)}{\alpha_m(1 - \alpha_m)}\left(\frac{d\alpha}{dt}\right)_m \tag{12}$$

and correspondingly:

$$E_n = \frac{nRT_m^2}{1 - \alpha_m} \cdot \left(\frac{d\alpha}{dt}\right)_m \tag{13}$$

A formal consideration of Eq. (12) indicates that at some finite value of the rate of transformation in the point α_m and T_m, for autocatalytically decomposing substances, the value of α_m must necessarily be higher than 0.5. In comparison with Eqs (12) and (13), the useful relationship $E_a \dfrac{\alpha_m}{2\alpha_m - 1}$ $vs.$ $\dfrac{E_n}{n}$ can be obtained. According to our work [7], the ratio E_n/n is a constant characteristic value for each factual kinetic curve.

References

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