Short Communication

A METHOD FOR DETERMINING THE STARTING TEMPERATURE OF THE THERMAL EFFECT

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A simple analytical method is suggested for determination of the starting temperature of the thermal effect. The method is based on the utilization of the kinetic characteristics of the transformation under investigation.

The starting temperature T_0 of the thermal effect is its most important characteristic [1 – 5]. However, its determination is connected in a complex manner with the methodology used by the observer, the resolution of the thermoanalytical instrument, the thermophysical properties of the material being studied, and the thermodynamic and kinetic characteristics of the transformation in question.

In the general case, one can always objectively separate three sections in one-stage transformations: the starting period, the transformation property, and its termination, which is usually accompanied by deceleration due to diffusion. Ultimately, it turns out that the kinetic equation reflecting the actual mechanism of the chemical reaction holds only over some intermediate part of the experimental kinetic curve. In this case the starting temperature of the transformation is sited with in the limiting area, and can obviously be subjected to substantial distortion. For this reason it is more correct to determine the temperature T_0 on the basis of the kinetic characteristics of the base line projection of the kinetic curve.

Let us consider some model for the thermal transformation of a substance which is assumed to follow the well-known kinetic equation:

$$\frac{d\alpha}{dt} = A_0 \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{1}$$

where the symbols are those usually applied.

In an earlier paper [6] it was demonstrated that the frequency factor A_0 in the Arrhenius equation can be expressed analytically in the following form:

$$A_0 = \frac{(1-\alpha_m)^{1-n}}{n} \cdot \frac{Eq}{RT_m^2} \exp\left(\frac{E}{RT_m}\right) \tag{2}$$

Hence, the rate constant of the observed transformation is

$$k = \frac{(1-\alpha_m)^{1-n}}{n} \cdot \frac{Eq}{RT_m^2} \exp\left(\frac{E}{RT_m}\right) \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where α_m is the conversion at the maximum rate of reaction, and q is the linear rate of temperature increase (degree $\cdot$ s^{-1}). Let us write the initial kinetic equation (1) in the following form:

$$\frac{d\alpha}{dT} = \frac{A_0}{q} \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{4}$$

An analysis of this equation demonstrates that the value $\frac{d\alpha}{dT}$ is formally independent from rate of temperature increase, as may be seen by substituting Eq. (3) into Eq. (4):

$$\frac{d\alpha}{dT} = \frac{E}{RT_m^2} \exp\left(\frac{E}{RT_m}\right) \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{5}$$

In the general case, the factor $\frac{(1-\alpha_m)^{1-n}}{n} \simeq 1$.

In the range of low conversions, Eq. (4) will assume a simpler form:

$$\left(\frac{d\alpha}{dT}\right)_0 = \frac{A_0}{q} \cdot \exp\left(-\frac{E}{RT}\right) \tag{6}$$

Hence, the fixed value $\left(\frac{d\alpha}{dT}\right)_0 = \theta$ may serve as a basis to draw conclusions on the starting temperature of the thermal effect. Piloyan and Kudinov did, in fact, suggest the assumption that $\left(\frac{d\alpha}{dT}\right)_0 = \frac{R}{E}$, from which they arrived at their equation [4, 5]:

$$T_0 = \frac{E}{R \ln \frac{A_0}{\theta q}} \quad \text{and} \quad T_{op} = \frac{E}{R \ln \frac{A_0 E}{Rq}} \tag{7}$$

The equation they proposed essentially corresponds to a level by agreement, for readings on the scale $\left(\frac{d\alpha}{dT}\right)_0$ at various values of $\frac{R}{E_i}$. However, such an approach to determine the starting temperature of the thermal effect does not satisfactorily ensure the conditions of standardization for a number of tested substances: there is no full agreement regarding the value α_0. Another factor causing inconvenience is the existence of the well-known compensation phenomenon of kinetic parameters, leading to variation in the value $\frac{R}{E_i}$. Essentially, the calculation of the starting temperature by means of the Piloyan–Kudinov equation may be useful for testing the thermal resistance of a substance under the effect of various factors [7].

Another approach for estimation of the starting temperature of the transformation or thermal effect consists in integrating Eq. (6) by the method described in [8]:

$$\int_0^{\alpha} \mathrm{d}\alpha = \frac{A_0}{q} \int_0^{T_0} \exp\left(-\frac{E}{RT}\right) \mathrm{d}T$$

This results in the basic equation for the calculation of the temperature T_0:

$$\alpha_0 = \frac{A_0}{q} \cdot \frac{RT_0^2}{E + 2RT_0} \exp\left(-\frac{E}{RT_0}\right) \tag{8}$$

If, on the basis of some concept, a standard value of α_0 is chosen, an electronic computer will readily yield the corresponding value of T_0. For calculations with a common calculator, however, it will be expedient to simplify Eq. (8) by substituting T_i for T_0:

$$\frac{RT_0^2}{E + 2RT_0} \simeq \frac{RT_i^2}{E + 2RT_i}$$

where T_i is the approximate starting temperature of the transformation or thermal effect, measured directly on the plot of the thermoanalytical curves by the observable deviation from the base line. With this treatment one finally arrives at the equation

$$T_0 = \frac{E}{R \ln \dfrac{A_0 RT_i^2}{\alpha_0 q(E + 2RT_i)}} \tag{9}$$

By way of example, let us consider the decomposition of calcium oxalate: $CaC_2O_4 \rightarrow CaCO_3 + CO$. The experimental data used were taken from [9]. The numerical values were $E = 250.9$ kJ/mol, $A_0 = 1.04 \cdot 10^{15}$ s^{-1}, $q = 10°$/min, $T_i = 676$ K. The calculated values for T_0 at various α_0 values are listed in Table 1. As regards the latter value, thermal analysts may agree on a standard value of 0.003.

Table 1

Temperature T_0 for the decomposition of calcium oxalate, calculated with various values of α_0

	$\alpha_0 = 0.01$	$\alpha_0 = 0.003$	$\alpha_0 = 0.001$	Calculated with the Piloyan-Kudinov equation]4, 5[
T_0	691 K	672 K	656 K	647 K

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