

TO THE PROBLEM OF APPLYING THE EQUATION OF
KOLMOGOROV, EROFEEV, KAZEEV, AVRAMI AND MAMPEL
TO THE KINETICS OF NON-ISOTHERMAL TRANSFORMATIONS

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The possibility of applying the KEKAM equation $-\ln(1 - \alpha) = kt^n$ to the kinetics of non-isothermal transformations is discussed. The derived form of this equation in the shape

$$\frac{d\alpha}{dt} = nk^{1/n}(1 - \alpha)[- \ln(1 - \alpha)]^{1-1/n},$$

according to the logic of the reasoning, cannot be applied to kinetic curves under the conditions of programmed heating.

One of the methods for the mathematical modeling of thermoanalytical and, correspondingly, thermokinetic curves in thermal analysis is the use of general kinetic equations deduced on the basis of model conceptions regarding the mechanism of the transformation in isothermal kinetics. An equation used for this purpose might be the well-known topochemical equation of Kolmogorov, Erofeev, Kazeev, Avrami and Mampel (abbreviated KEKAM)

$$-\ln(1 - \alpha) = kt^n. \tag{1}$$

This equation is of particular interest for kinetic analyses aiming to determine the value of the exponent n , its knowledge allowing to find the limiting stages of the transformation [1–3]. The correspondence between the conversion α_m and the value n in the point where the speed of transformation is highest is demonstrated by the following figures:

n	1	1.28	2.04	3.22	11.1	-5	-1.67
α_m	0	0.2	0.4	0.5	0.6	0.7	0.8

Equation (1) can be presented in the derived forms

$$\frac{d\alpha}{dt} = nkt^{n-1}(1 - \alpha) \tag{2a}$$

$$\frac{d\alpha}{dt} = \frac{n}{t}(1 - \alpha)[- \ln(1 - \alpha)] \tag{2b}$$

$$\frac{d\alpha}{dt} = nk^{1/n}(1 - \alpha)[- \ln(1 - \alpha)]^{1-1/n}. \tag{2c}$$

Among these, only Eq. (2a) can be used to describe non-isothermal transformations. In fact, after the logarithmation of Eq. (1) and subsequent derivation, Eq. (2b) is obtained, whereby $\frac{d \ln k}{dt} = 0$ and hence the rate constant k will be eliminated. Eq. (2c) is the derivative of Eq. (2b).

In addition to the usual kinetic interpretation, the starting equation Eq. (1) can be regarded as the probability function of the dwelling time in the unreacted state of the substance investigated, under the chosen experimental conditions [5].

For non-isothermal conditions, at $n = \text{const.}$ and $k = k_0 \exp\left(-\frac{E}{RT}\right)$ it may be presented as

$$P = (1 - \alpha) = \exp(-kt^n) = \exp(-k_0\Theta^n) \quad (3)$$

where $\Theta = t \exp\left(-\frac{E}{nRT}\right)$.

If, to describe the non-isothermal curve, one starts from the derived kinetic equation Eq. (2a) at linear programming of temperature, i.e. $T = T_0 + at$, the following expression will be obtained:

$$\frac{d\alpha}{dt} = nk_0 \left(\frac{T - T_0}{a}\right)^{n-1} \exp\left(-\frac{E}{RT}\right) (1 - \alpha). \quad (4)$$

Integration of this equation at the condition $T \gg T_0$ according to [6] results in

$$-\ln(1 - \alpha) = \frac{nk_0}{a^n} \cdot \frac{RT^{n+1}}{E + (n+1)RT} \exp\left(-\frac{E}{RT}\right). \quad (5)$$

If it is considered that the value $\frac{nk_0RT}{[E + (n+1)RT]a^n}$ varies only slightly within the temperature range of the transformation investigated, one obtains, after logarithmation

$$\ln[-\ln(1 - \alpha)] = -\frac{E}{RT} + n \ln T + \text{const.} \quad (6)$$

Consequently, in order to establish the activation energy value E , the preliminary knowledge of the kinetic exponent n is indispensable. This value can be evaluated by selection using a computer.

Earlier [7] we suggested a procedure to determine the value \bar{n} for Eq. (3) within some interval of conversion $\alpha_1(t_1)$ and $\alpha_2(t_2)$ by means of the formula

$$\bar{n} = \frac{\ln \left\{ \frac{[-\ln(1 - \alpha_{\text{med}})]^2}{[-\ln(1 - \alpha_1)][-\ln(1 - \alpha_2)]} \right\}}{\ln \left(\frac{t_{\text{med}}^2}{t_1 t_2} \right)}$$

where $\alpha_{\text{med}}(t_{\text{med}})$ is an intermediate value, satisfying the condition

$$\frac{T_{\text{med}} - T_1}{T_{\text{med}} \cdot T_1} = \frac{T_2 - T_{\text{med}}}{T_2 \cdot T_{\text{med}}}.$$

However, this procedure is sensitive to the width that the kinetic curve spans, that is, narrowing of the interval $\alpha_1 \dots \alpha_2$ will lead to indefiniteness, and may, in certain cases, yield results lacking physical meaning. The latter circumstance may indicate that the kinetic curve in question cannot be modeled by means of Eq. (1). By all accounts, the above procedure must still be confirmed by a satisfactorily large experimental material.

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