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# REMARKS ON THE APPLICATION OF THE COMBINED KOLMOGOROV–EROFEEV–KAZEEV–AVRAMI–MAMPEL EQUATION IN THE KINETICS OF NON-ISOTHERMAL TRANSFORMATIONS

V. M. GORBACHEV

*Institute of Inorganic Chemistry, Sibirian Department of the Academy of Sciences of the U. S. S. R., Novosibirsk 630090*

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The possibility of using the KEKAM equation $\alpha = 1 - \exp(-kt^n)$ in the kinetics of non-isothermal transformations is discussed. Calculation methods are proposed for the determination of the kinetic exponent $n$ from thermoanalytical curves within a chosen temperature range.

It is a prevalent trend in our days to gather information, both in theoretical and practical studies, on the kinetics and on the assumed mechanism of non-isothermal transformations by the computerized analysis of some set of kinetic equations based on some accepted model conception concerning the course of the solid-state chemical reaction [1, 2]. The kinetic characteristics obtained after computations (the activation energy $E$ of the reaction, the pre-exponential factor $k_0$ in the Arrhenius equation, and the mechanism function $f(\alpha)$ of the reaction) are presumed to have a real physical meaning. However, a fact known from the experience of isothermal kinetics must be borne in mind, namely that the true, existing kinetic curve may formally be described by a number of kinetic equations based on different or even contradictory model conceptions [3]. If, on the other hand, the kinetic curve in question cannot be described by a given kinetic equation, then the corresponding model may with certainty be excluded from considerations. However, it should be mentioned here that the kinetic characteristics ($E$ and $k_0$) obtained in isothermal kinetics by using different kinetic equations frequently differ only slightly [3].

The situation is quite different in non-isothermal kinetics, where the kinetic characteristics $E$ and $k_0$ largely depend on the form of the kinetic equation taken into account [4]:

$$\frac{d\alpha}{dt} = K(T) \cdot f(\alpha) \qquad (1)$$

and also on the chosen temperature program [5].

This difficulty can be avoided by deliberately using a more general kinetic equation for the calculation of the kinetic characteristics all the rest following from this equation. The combined Kolmogorov–Erofeev–Kazeev–Avrami–Mampel equation (abbreviated KEKAM) [6–10] is one of these general equations:

$$\alpha = 1 - \exp(-Kt^n). \qquad (2)$$

The differential form of the KEKAM equation under isothermal conditions is:

$$\frac{\mathrm{d}}{\mathrm{d}t} = nk^{1/n} \cdot (1 - \alpha) \; [-\ln (1 - \alpha)]^{1-1/n}. \tag{3}$$

Basically, the starting equation (2) is derived from topochemical considerations on the course of chemical reactions in isothermal conditions. Kazeev [8] derived this equation from concepts of the theory of similarity and succesfully applied it to describe a wide range of chemical reactions. Voldman [11] demonstrated that the kinetic exponent $n$ in Eq. (2) does not always necessarily have a topochemical meaning. In our opinion, the KEKAM equation, in the most general case, may be considered as the function of the a posteriori probability of the degree of transformation. By determining from experimental data the corresponding kinetic (or probability) characteristics $k$ and $n$, one will, in the majority of cases, succeed in describing the actual kinetic curve, disregarding – as a first approach – the actual mechanisms of the transformation. In addition, lately the potentials of the formal-kinetic analysis based on the KEKAM equation have substantially increased, as a result of finding the compensation relationship [12–14] between the kinetic parameters $k$ and $n$:

$$\ln k = a - bn. \tag{4}$$

The values of $k$ and $n$ may change owing to a number of causes: dispersity of the starting solid material, defects in the crystal lattice, change in the number of the potential centres of the reaction, effected by external factors: method of preparing the starting material, preliminary thermal treatment, effect of radiation, ageing of the specimen etc. For the decomposition of a given substance, the joint variation of the kinetic parameters $k$ and $n$ will finally be limited by the compensation relationship in the form of Eq.(4).

To describe the kinetic curves under the conditions of programmed heating, the KEKAM equation may, on principle, be applied, assuming that the kinetic parameters $k$ and $n$ change with temperature according to the Arrhenius equation:

$$k = k_0 \exp(-E/RT) \text{ and } n = n_0 \exp(-\varepsilon/RT). \tag{5}$$

The use of Eq. (2) in non-isothermal kinetics in the general case is already known in the literature [15–17], but its use has not specially been analyzed. In the followings, the application of the KEKAM equation will be considered in more detail for linear, exponential and hyperbolic heating, assuming that the kinetic exponent $n$ changes little with temperature, and hence, over a certain temperature range, it may be replaced by the constant $\bar{n}$.

Let us write the initial equation (2) in the following form:

$$-\ln (1 - \alpha) = k_0 \exp(-E/RT)\, t^{\bar{n}} \tag{6}$$

or in the logarithmic form:

$$\ln [-\ln(1 - \alpha)] = -E/RT + \bar{n} \ln t + \ln k_0. \tag{7}$$

Under the conditions of a non-isothermal course of the transformation process, the temperature functionally related to time by the given program is
(i) linear: $T = T_0 + \beta t$
(ii) exponential: $T = T_0 \exp \sigma t$
(iii) hyperbolic: $1/T = 1/T_0 - \eta t$.

Differentiation of Eq. (7) yields

$$E = \frac{RT^2(\mathrm{d}\alpha/\mathrm{d}t)}{q(1-\alpha)[-\ln(1-\alpha)]} - \frac{\bar{n}RT^2}{tq} \tag{8}$$

where $q = \mathrm{d}T/\mathrm{d}t$ is the rate of temperature increase in all points of the kinetic curve. For linear heating $q = \beta$. From Eq.(8), an interesting conclusion can be made regarding the possibility to estimate the value of the activation energy in every point of the thermokinetic curve, under the condition that the kinetic exponent $n$ is *a priori* known (or at least some mean value $\bar{n}$ in the temperature range in question), and the transformation rate in every moment is accurately determined.

Several computation methods for determining the mean value $\bar{n}$ over the chosen transformation range from $\alpha(T_1)$ to $\alpha(T_2)$ can be proposed, if it is assumed that the activation energy $E$ is constant within this range. For linear heating, Eq. (8) will yield

$$\bar{n} = \frac{\dfrac{T_1^2(\mathrm{d}\alpha/\mathrm{d}t)_1}{(1-\alpha_1)[-\ln(1-\alpha_1)]} - \dfrac{T_2^2(\mathrm{d}\alpha/\mathrm{d}t)_2}{(1-\alpha_2)[-\ln(1-\alpha_2)]}}{T_1^2/t_1 - T_2^2/t_2} \tag{9}$$

and for non-linear temperature programs:

$$\bar{n} = \frac{\dfrac{T_1^2(\mathrm{d}\alpha/\mathrm{d}t)_1}{q_1(1-\alpha_1)[-\ln(1-\alpha_1)]} - \dfrac{T_2^2(\mathrm{d}\alpha/\mathrm{d}t)_2}{q_2(1-\alpha_2)[-\ln(1-\alpha_2)]}}{T_1^2/t_1q_1 - T_2^2/t_2q_2}. \tag{10}$$

Let us now consider another method for the determination of the kinetic exponent, utilizing only one integral thermokinetic curve within the limits $\alpha(T_1)$ and $\alpha(T_2)$, with $\alpha(T_m)$ symbolizing maximum rate of transformation. For this case, the following set of equations can be written:

$$\begin{aligned} \frac{\ln(1-\alpha_m)}{\ln(1-\alpha_1)} &= (t_m/t_1)^{\bar{n}} \cdot \exp(-E/RT_m + E/RT_1) \\ \frac{\ln(1-\alpha_2)}{\ln(1-\alpha_m)} &= (t_2/t_m)^{\bar{n}} \cdot \exp(-E/RT_2 + E/RT_m). \end{aligned} \tag{11}$$

On principle, one can always chose such values for $T_1$ and $T_2$ that the following relationship be satisfied:

$$\frac{T_m - T_1}{T_m \cdot T_1} = \frac{T_2 - T_m}{T_2 \cdot T_m}.$$

After having chosen the temperature $T_1$ out of certain considerations, the conjugate temperature $T_2$ can be determined analytically:

$$T_2 = \frac{T_1 \cdot T_m}{2T_1 - T_m} . \tag{12}$$

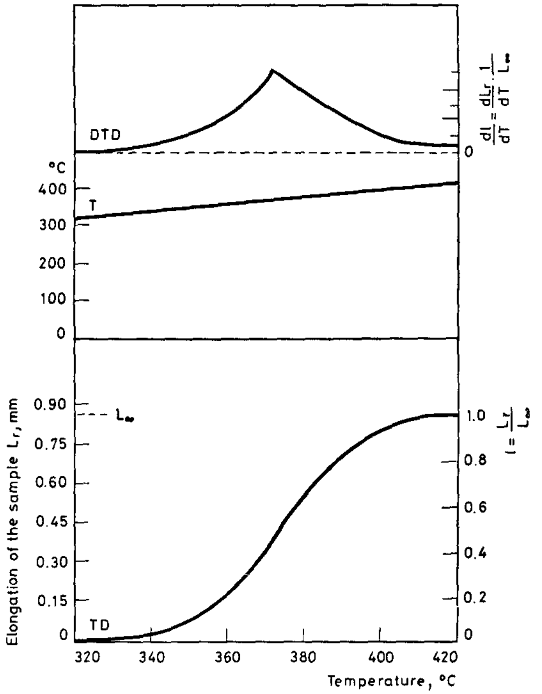

Fig. 1. Dilatometric curve of aragonite

Taking into account this condition, the set of Eq.(11) can be transformed into a simple expression to determine $\bar{n}$:

$$\bar{n} = \frac{\ln\left\{\dfrac{[-\ln(1-\alpha_m)]^2}{[-\ln(1-\alpha_1)]\,[-\ln(1-\alpha_2)]}\right\}}{\ln t_m^2/t_1 \cdot t_2} . \tag{13}$$

By way of example for the proposed method, let us consider calculation of the kinetic constants of the transformation of aragonite into calcite by means of the dilatometric curve [18] reproduced in Fig. 1. For a linear temperature increase rate of 4°/min and a starting temperature of the transformation $T_0 = 593$ K, the following basic data for the calculation can be obtained from the thermodilatogram:

$$\begin{array}{rlrlrl} T_1 &= 633\ \text{K} & T_m &= 644\ \text{K} & T_2 &= 655\ \text{K}. \\ 1 - \alpha_1 &= 0.80 & 1 - \alpha_m &= 0.57 & 1 - \alpha_2 &= 0.27 \\ t_1 &= 10\ \text{min} & t_m &= 12.75\ \text{min} & t_2 &= 15.5\ \text{min} \end{array}$$

By introducing these data into Eq.(13), the kinetic exponent $\bar{n} = 1$ is obtained. For the activation energy over the temperature range $T_1$ to $T_2$, the formula

$$\frac{\ln(1-\alpha_1)}{\ln(1-\alpha_2)} = \frac{T_1 - T_0}{T_2 - T_0} \exp\left(E/RT_2 - E/RT_1\right)$$

yields the value $E = 49$ kcal/mol, being identical with the literature value reported in [18] and $k = 1.6 \cdot 10^{14}\ \text{sec}^{-1}$.

The calculation of the kinetic characteristics from a single differential dilatometric curve using Eqs (8) and (9) yields unsatisfactory results, owing to the objectionable transformation of the TD curve into the DTD curve in the given experiment.

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Résumé — On discute la possibilité d'appliquer l'équation de KEKAM $\alpha = 1 - \exp(-kt^n)$ à la cinétique des transformations non isothermes. On propose des méthodes de calcul pour déterminer l'exposant cinétique $n$ à partir des courbes thermoanalytiques, dans un intervalle choisi de température.

Zusammenfassung — Die Möglichkeit der Anwendung der KEKAM-Gleichung $\alpha = 1 - \exp(-kt^n)$ bei der Kinetik nicht-isothermer Umwandlungen wird beschrieben. Berechnungsmethoden zur Bestimmung des kinetischen Exponenten $n$ aus thermoanalytischen Daten in einem gewählten Temperaturbereich werden vorgeschlagen.

Резюме — Обсуждается возможность использования уравнения КЕКАМ $\alpha = 1\text{-}\exp(\text{-}kt^n)$ в кинетике неизотермических превращений. Предлагаются расчетные методы определения кинетического показателя $n$ из термоаналитических кривых внутри выбранного температурного интервала.