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

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An analysis is made of the method proposed by Gorbachev for the kinetic study of non-isothermal transformations using the KEKAM equation $\alpha = 1 - \exp(-kt^n)$. It is demonstrated that the procedure cannot be used to determine either the kinetic exponent n or the activation energy E.

In a very recent paper Gorbachev [1] proposes the use of the Kolmogorov-Erofeev-Kazeev-Avrami-Mampel law (abbreviated KEKAM):

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

as a general equation to determine the activation energy of solid-state reactions from data obtained under a linear heating program for temperature increase. For this purpose, after taking into account the Arrhenius law, Gorbachev writes Eq. (1) in the following form:

$$-\ln(1-\alpha) = A\exp(-E/RT)t^n \tag{2}$$

α being the reacted fraction, A the pre-exponential Arrhenius factor, E the activation energy, T the absolute temperature, t the time from the start of the reaction, and n a constant that it is assumed to change little with temperature.

By using the integral thermokinetic curve within the limits $\alpha(T_1)$ and $\alpha(T_2)$, with $\alpha(T_m)$ symbolizing the point of the curve with maximum rate of transformation he found the following set of equations:

$$\frac{\ln(1-\alpha_m)}{\ln(1-\alpha_1)} = \left(\frac{t_m}{t_1}\right)^n \exp(-E/RT_m + E/RT_1) \tag{3a}$$

$$\frac{\ln(1-\alpha_2)}{\ln(1-\alpha_m)} = \left(\frac{t_2}{t_m}\right)^n \exp(-E/RT_2 + E/RT_m) \tag{3b}$$

and, after considering that $t_1 = (T_1 - T_0)/\beta$, $t_2 = (T_2 - T_0)/\beta$ and $t_m = (T_m - T_0)/\beta$ (β being the heating rate), he obtains [Eq. (4) from Eqs (3a) and 3b):

$$\frac{\ln(1-\alpha_1)}{\ln(1-\alpha_2)} = \left[\frac{T_1 - T_0}{T_2 - T_0}\right]^n \exp(E/RT_2 - E/RT_1) \tag{4}$$

On the other hand, Gorbachev considers that it is always possible to choose values for T_1 and T_2 that satisfy the relationship:

$$\frac{T_m - T_1}{T_m T_1} = \frac{T_2 - T_m}{T_2 T_m} \tag{5a}$$

In other words, once the temperature T_1 is selected, the conjugate temperature T_2 can be determined from:

$$T_2 = \frac{T_1 T_m}{2T_1 - T_m} \tag{5b}$$

and taking into account this condition, he obtains the expression (6) from the set of equations (3a) and (3b):

$$n = \frac{\ln\left[\frac{[-\ln(1-\alpha_m)]^2}{[-\ln(1-\alpha_1)][-\ln(1-\alpha_2)]}\right]}{\ln(t_m^2/t_1 t_2)} \tag{6}$$

On these grounds, Gorbachev suggests a method of kinetic analysis that involves determination of n from Eq. (6) and then the activation energy from Eq. (4).

By way of example, the proposed method is applied [1] to calculate the kinetic constants of transformation of aragonite into calcite from a dilatometric curve recorded at a heating rate of 4°/min. Under these conditions the starting temperature reported for the transformation was $T_0 = 593$ K and the maximum reaction rate was reached at $T_m = 644$ K, when the fraction reacted was $\alpha_m = 0.43$. Therefore selecting from the thermodilatometric curve the basic data $T_1 = 633$ K, $(1 - \alpha_1) = 0.80$, $T_2 = 655$ K, and $(1 - \alpha_2) = 0.27$, Gorbachev found from Eqs (6) and (4) an exponent $n = 1$ and an activation energy $E = 49$ kcal/mol.

The aim of the present paper is to show that the method of calculation of kinetic parameters based upon Eqs (4) and (6) has no real meaning and leads to serious errors in the determination of both n and E. In fact, if we select from the dilatometric curve plotted in Fig. 1 of Gorbachev's paper [1] any temperature T_1 different from that used by the author, quite different values of n and E are obtained, as shown in Table 1.

The reason for the dispersion of the results included in this table is that Eq. (3) cannot be used for carrying out the kinetic analysis of non-isothermal data. This is due to the fact that the differential form of the kinetic equations cannot be integrated without previously taking into account the mathematical function that relates the temperature with the time.

It is well known [1] that the differential form of the KEKAM equation under isothermal conditions is:

$$\frac{d\alpha}{dt} = nk^{1/n}(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{7}$$

and that under non-isothermal conditions it becomes:

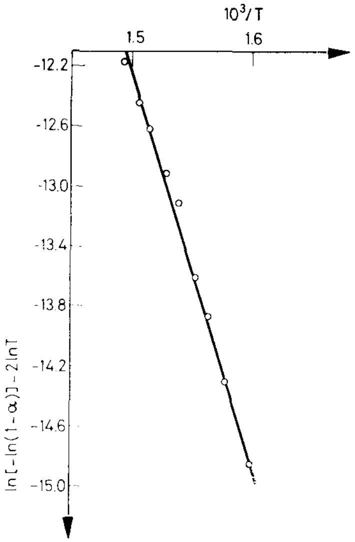

Fig. 1. Plot of the data on the aragonite → calcite transformation included in ref. [1] according to Eq. (10) (α range: $0.13 \leq \alpha \leq 0.90$)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = nA^{1/n}\exp(-E/nRT)\cdot(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{8}$$

If a linear temperature increase rate $\beta = \mathrm{d}T/\mathrm{d}t$ is used to perform the kinetic analysis, we can integrate Eq. (8), following previous papers (2), (3) and we obtain:

$$[-\ln(1-\alpha)]^{1/n} = \frac{nA^{1/n}RT^2}{E\beta}\exp(-E/nRT) \tag{9}$$

Table 1

Calculation of n and E for the transformation aragonite → calcite by means of Eqs (6) and (4)

$T_0 = 593$ K; $T_m = 644$ K; $(1-\alpha_m) = 0.57$; $\beta = 4$ °/min

T_1, K	$(1-\alpha_1)$	T_2 K	$(1-\alpha_2)$	n	E kcal/mol
635	0.76	653	0.35	3	12
637	0.71	651	0.39	−1	76
639	0.68	649	0.43	−3	113
641	0.63	647	0.49	−12	254

* Data taken from the thermodilatometric curve reported in ref. [1]

Rearranged in logarithmic form, this becomes:

$$\ln[-\ln(1-\alpha)] - 2n\ln T = n\ln\frac{nA^{1/n}R}{E\beta} - \frac{E}{RT} \tag{10}$$

A plot of the left hand side of Eq. (10) against $1/T$ would yield a straight line whose slope gives the activation energy of the process.

Therefore, we must conclude that Eq. (10) should be used instead of Eqs (4) and (6) to perform the kinetic analysis of data obtained under a linear heating program by means of the KEKAM law.

In fact, the data reported in [1] for the transformation aragonite → calcite are plotted in Fig. 1 according to Eq. (10), after assuming $n = 1$. A very good linear correlation coefficient ($r = 0.9949$) and an activation energy $E = 51$ kcal/mol are obtained. If we were to assume $n = 2$ or $n = 3$, very similar activation energies would be obtained (50 kcal/mol and 48 kcal/mol. respectively), but the correlation coefficients would be poorer ($r = 0.9934$ and $r = 0.9926$, respectively).

References

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