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COMPLEMENTARITY METHODOLOGY AS APPLIED FOR SOLUTION OF THE INVERSE PROBLEM OF SOLID-PHASE REACTION KINETICS

Part I. Interpretation of the Applicability of the Generalized Topokinetic Equation for Describing Complex Processes

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The possibility of describing complex processes by means of the KEKAM equation is demonstrated. The extensive descriptive ability of this equation can be explained within the nontraditional methodology of inverse kinetic problem solving.

In paper [1] the nontraditional methodology of solving the inverse kinetic problem is considered. In contrast to the traditional procedure based on the principle of an unambiguous description, which of necessity requires the choice of single kinetic function for the entire kinetic curve or for its segments, the nontraditional methodology relies upon the complementary principle and uses a totality of, rather than separate kinetic functions for the same segment of the kinetic curve. Two particular approaches to the inverse problem solution within the nontraditional methodology have been considered in [2, 3]. The present series discusses other possible approaches.

The first part of the series explains the extensive descriptive ability [4] of the generalized topokinetic equation of Kolmogorov–Erofeev–Kazeev–Avrami–Mampel (KEKAM) and substantiates its application within the nontraditional methodology. The expression extensive ability here means the ability of the KEKAM equation to describe not only nucleation and nuclear growth, but also processes of a different nature. In the latter case, a physically based interpretation of experimental data in terms of the KEKAM models seems impossible.

It is convincingly demonstrated in [5] that the KEKAM equation can fairly well reflect elementary reaction mechanism models different from the physical model

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involved in this equation and corresponding to other kinetic functions. The KEKAM equation, however, can cover not only elementary, but also rather complex models of a process, which for example conform with the linear combination of kinetic functions. This will be shown in what follows. Theoretically, this linear combination describes the process, which consists of a number of parallel reactions with close activation energies.

As the linear combination, we have used functions of three classes not reducible to one another [3], corresponding to power law nuclear growth ($f_1(\alpha)$), a phase boundary reaction ($f_2(\alpha)$) and diffusion ($f_3(\alpha)$). The approximation problem reduces mathematically to finding the coefficients of Eq. (1) for each prescribed value of the exponent in the KEKAM equation:

$$[-\ln(1-\alpha)]^{1/m} = C_1 f_1(\alpha) + C_2 f_2(\alpha) + C_3 f_3(\alpha) \tag{1}$$

It is evident that, when α is prescribed, the coefficients C_1, C_2 and C_3 in Eq. (1) may be found by using the least squares method, i.e. from the condition of minimum (2):

$$\sum_{i=1}^{k} ([-\ln(1-\alpha_i)]^{1/m} - C_1 f_1(\alpha_i) - C_2 f_2(\alpha_i) - C_3 f_3(\alpha_i))^2 \tag{2}$$

where k is the number of transformation degree values; i is their ordinal number. As (2) is linear relative to the coefficients, the latter can be found by using ordinary multiple linear regression [6]. The approximation quality is characterized by the mean relative deviation, calculated as

$$\delta = \frac{100}{k} \sum_{i=1}^{k} \left| \frac{[-\ln(1-\alpha_i)]^{1/m} - C_1 f_1(\alpha_i) - C_2 f_2(\alpha_i) - C_3 f_3(\alpha_i)}{[-\ln(1-\alpha_i)]^{1/m}} \right| \tag{3}$$

The coefficients of Eq. (1), calculated for five different values of m (Eqs (4) through (8)), are given below as an example. The base functions of the linear combination ($f_1(\alpha), f_2(\alpha)$ and $f_3(\alpha)$) are chosen arbitrarily within the above classes. Ten equidistant values of α from the range 0.01 to 0.9 were used for calculation, the greatest deviations (to 10δ) being observed at $\alpha < 0.1$.

$$[-\ln(1-\alpha)]^{1/4} \approx C_1\alpha^{1/4} + C_2[1-(1-\alpha)^{1/2}] + C_3[1-(1-\alpha)^{1/3}]^2 \tag{4}$$

$C_1 = 0.99 \qquad C_2 = 0.194 \qquad C_3 = 0.45 \qquad \delta = 0.07\%$

$$[-\ln(1-\alpha)]^{1/3} \approx C_1\alpha^{1/3} + C_2[1-(1-\alpha)^{1/3}] + C_3[1-(1-\alpha)^{1\infty 3}]^2 \tag{5}$$

$C_1 = 1.0 \qquad C_2 = 0.3 \qquad C_3 = 0.675 \qquad \delta = 0.1\%$

$$[-\ln(1-\alpha)]^{1/2} \approx C_1\alpha^{1/2} + C_2[1-(1-\alpha)^{1/2}] + C_3[1-(1-\alpha)^{1/3}]^2 \tag{6}$$

$C_1 = 0.97 \qquad C_2 = 0.3 \qquad C_3 = 1.365 \qquad \delta = 0.2\%$

$$[-\ln(1-\alpha)]^{2/3} \approx C_1\alpha^{2/3} + C_2[1-(1-\alpha)^{1/2}] + C_3[1-(1-\alpha)^{1/3}]^2 \quad (7)$$

$C_1 = 0.5$ $C_2 = 2.4$ $C_3 = 3.75$ $\delta = 0.4\%$

$$[-\ln(1-\alpha)] \approx C_1\alpha + C_2[1-(1-\alpha)^{1/2}] + C_3[1-(1-\alpha)^{1/3}]^2 \quad (8)$$

$C_1 = 2.41$ $C_2 = -2.8$ $C_3 = 7.05$ $\delta = 0.5\%$

The values of δ for Eqs(4) through (8) indicate that the above approximations are satisfactory, and suggest two calculations. First, the KEKAM equation can describe both elementary reaction mechanism models obeying one kinetic function and complex processes obeying a linear combination of functions. Thus, it provides a generalized description of different solid-phase processes. Second, the class of KEKAM functions within some error is redundant, since any function of this class can be replaced by a linear combination of three other classes [3]. The KEKAM functiones redundancy follows from [7] too, where the undistinguishedness of its particular forms in a single non-isothermal experiment is mentioned. Therefore a complex solid-phase process can formally be described either through a set of linearly independent kinetic functions not belonging to the class of KEKAM functions but reflecting one of the important process features, or in terms of one KEKAM function providing a generalized description. It should be noted that in the former case the problem of discriminating the competing kinetic functions inevitably arises, and cannot be solved unambiguously by formal means [1], while in the latter case it is required to find the KEKAM function parameter that will best describe the process (but its value may be not physically interpreted) and the corresponding confidence boundaries. Then the effective values of the activation energy and preexponential factor can be found. Everything stated above relates not only to the KEKAM functions, but also to other functions proposed as generalized ones, e.g. in [8, 9]. The reliability and practical value of the effective kinetic parameters obtained by means of generalized description functions depend upon the certainty with which this function approximates to the kinetic curve.

Conclusion

(i) The extensive descriptive ability of the KEKAM equation can be explained within the nontraditional methodology [1] of solving the inverse kinetic problem.

(ii) Since the main difference of the nontraditional methodology from the traditional one implies the use of a generalized rather than a single kinetic function for the description of a process, then, because of (i), the application of even a single KEKAM function (or one similar to this) to describe complex processes, i.e. those

which do not consist with the KEKAM models, may be considered to some approximation as a description within the framework of the nontraditional methodology.

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Zusammenfassung — Die Moglichkeit einer komplexen Prozeßbeschreibung mittels der KEKAM-Gleichung wird demonstriert Die umfassende Eignung dieser Gleichung kann mit der nichttraditionellen Methodologie der Losung inverser kinetischer Probleme erklart werden.

Резюме — Продемонстрирована возможность описания сложных процессов с помощью уравнения КЕКАМ. Широкая описательная способность этого уравнения может быть объяснена в рамках нетрадиционной методологии решения обратной кинетической задачи.