

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

Generalized kinetic description using a spectrum of functions

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A method is suggested for a generalized kinetic description of solid-phase processes on the basis of the complementarity principle. It enables one to obtain spectra as discrete distributions of the probability of describing a process in terms of kinetic functions according to their ordinal numbers. The spectra obtained make it possible to control changes in the behaviour of a solid-phase process due to changing process conditions.

It has been shown in part I [1] that the KEKAM (Kolmogorov–Erofeev–Kazeev–Avrami–Mampel) equation used in the kinetics of solid-phase processes possesses the features of a generalized description peculiar to the nontraditional approach [2] to the solution of the inverse kinetic problem. The present part deals with a new method of such an approach, using the probability spectra of kinetic functions for a generalized description of a process. Further, the specificities and applications of the method are considered.

Probability spectra of kinetic functions

It is clear that an experimental kinetic curve may be described by various formal models (kinetic functions) within different accuracies characterized by the correlation coefficients or residual squared sums. These values are essentially a statistical form for the probability of describing a kinetic curve in terms of a kinetic function. The probability spectrum of kinetic functions is therefore understood to be a discrete distribution of the probabilities of describing the kinetic curve with kinetic functions in accordance with their ordinal numbers (Table 1).

Table 1 Formal models of solid-phase processes

<i>N</i>	Formal model		<i>g</i> (α)
1			$\alpha^{1/4}$
2			$\alpha^{1/3}$
3		Power law	$\alpha^{1/2}$
4			α
5			$\alpha^{3/2}$
6	Contracting geometry	Cylinder	$2[1 - (1 - \alpha)^{1/2}]$
7		Sphere	$3[1 - (1 - \alpha)^{1/3}]$
8		Mampel	$-\ln(1 - \alpha)$
9		Reaction order	$(1 - \alpha)^{-1/2} - 1$
10			$(1 - \alpha)^{-1} - 1$
11		Anti-jander	$1.5[(1 + \alpha)^{1/3} - 1]^2$
12		One-dimensional	α^2
13	Diffusion	Valensi	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
14		Ginstling-Brounstein	$1.5 \left[1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} \right]$
15		Jander	$1.5[1 - (1 - \alpha)^{1/3}]^2$

The description probabilities were calculated through residual dispersions obtained by the least squares method for each of the kinetic functions substituted into the Coats-Redfern equation [3]. The probability calculation method is considered in detail in [4]. Upon calculation, the probability values are presented as

percentages of the maximum value. The final form of the spectrum is $\frac{p_i}{p_{\max}} \cdot 100\%$ vs. i , where p_i is the description probability with the use of the i -th kinetic function, p_{\max} is the maximum value of all p_i , and i is the ordinal number of the kinetic function.

For spectra calculations, the kinetic functions of Table 1 have been used. The KEKAM-type equations were disregarded, as they may be replaced within some error by a linear combination of functions of three other classes [5] describing the power law of nuclear growth, interface reaction and diffusion. Hence, the KEKAM-type equations cannot give any additional information when the entire set of kinetic functions of the above three classes is used.

Function spectrum properties

In the case of accurate experiments, the kinetic curves are rather smooth, i.e. the random error is small. Therefore, when describing fairly smooth experimental

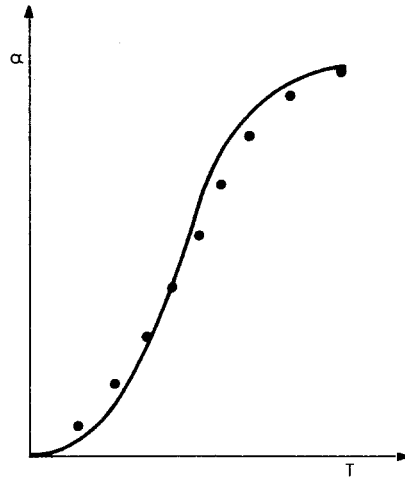


Fig. 1 Regular displacement of theoretical curves relative to the experimental points

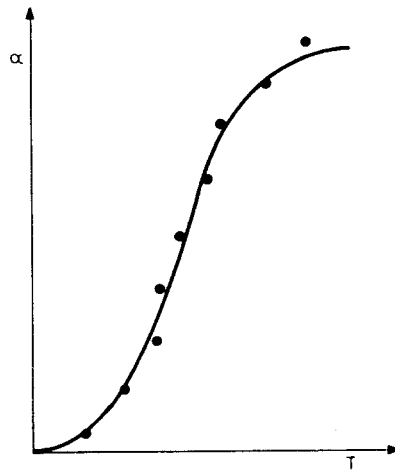


Fig. 2 Random scatter of experimental points around the theoretical curves

relationships by perfectly smooth model curves, one encounters primarily systematic, rather than random errors, which appear because none of the real kinetic curves exactly coincide with the theoretical one. This results in the regular displacement of the theoretical curves relative to the experimental relationship (Fig. 1), but not in the random scatter of the experimental points around the theoretical curve (Fig. 2). Thus, if the variation of the experimental conditions does not change the behaviour of the experimental curve, then equivalent shifts of the theoretical curves relative to the experimental one will be observed at equivalent curve points

(for example, for equal decomposition degree) characterizing different experimental conditions. This finally results in equivalent relationships between the appropriate description probabilities for experimental dependences obtained for different experimental conditions, i.e. in actually equivalent spectra.

Hence, the spectra of kinetic functions must be invariant to changing experimental conditions (first of all temperature under isothermal conditions, and heating rate under nonisothermal conditions) if no qualitative changes are encountered in the process behaviour. Otherwise, the form of the spectra will inevitably change.

Experimental data modelling

Kinetic curves were modelled for isothermal conditions in accordance with Eq. (1):

$$\alpha = G\left(A \cdot \exp\left(-\frac{E}{RT}\right)t\right) \quad (1)$$

and for nonisothermal conditions in accordance with Eq. (2):

$$\alpha = G\left(\frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT\right) \quad (2)$$

where G is the inverse of the kinetic functions for $g(\alpha)$, i.e.

$$G(g(\alpha)) = \alpha \quad (3)$$

The integral in (2) was replaced by the approximation suggested in [6]:

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E \exp(-x)}{R} \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (4)$$

where $x = \frac{E}{RT}$.

A linear combination of two kinetic functions (N7 and N15, Table 1) describing the interface reaction (spherical symmetry) and diffusion (Jander equation) was chosen as $g(\alpha)$:

$$g(\alpha) = c_1 \cdot 3[1 - (1 - \alpha)^{1/3}] + c_2 \frac{3}{2}[1 - (1 - \alpha)^{1/3}]^2 \quad (5)$$

Such a choice is stipulated by two main reasons. First, Eq. (5) determines the complex kinetics. Thus, the experimental data obtained with its aid might not coincide with any of the simple models. If this condition is not obeyed, the spectrum

of the simulated process will acquire a trivial form, being one 100% line. Second, there exists a very simple inverse function G for function (5):

$$\alpha = 1 - \left(1 + \frac{c_1}{c_2} \pm \sqrt{\left(\frac{c_1}{c_2}\right)^2 + \frac{2g(\alpha)}{3c_2}} \right)^3 \quad (6)$$

Equations (1) and (2) were used to find the values of time (isothermal conditions) and temperature (nonisothermal conditions) consistent with the decomposition degrees 0.1, 0.2, ..., 0.9 and different C_1 and C_2 combinations in (5), such as 0.3:0.7, 0.5:0.5 and 0.7:0.3. The spectra obtained with isothermal data for five temperatures (350, 355, 360, 365 and 370 K) are essentially equivalent at prescribed C_1 and C_2 , and are of the form presented in Fig. 3. The spectra obtained with nonisothermal data for five heating rates (1.25, 2.5, 5.0, 10.0 and 20.0 deg · min⁻¹) are also equivalent for prescribed C_1 and C_2 (Fig. 4).

From comparison of the spectra for one and the same process under isothermal and nonisothermal conditions, it can easily be seen that in the latter case the spectrum is of more complicated form. This fact presumably stems from the complication of the non-isothermal kinetic curve due to the temperature-dependence of the exponential part of Eq. (2). Such complication in particular is responsible for the fact that the discrimination of kinetic functions in terms of nonisothermal data is always more complex than it is in the isothermal case.

It should be also emphasized that the strongest lines in the spectra of processes prescribed by linear combination (5) in the general case do not conform with the kinetic functions N7 and N15 (Table 1) in either the isothermal or the

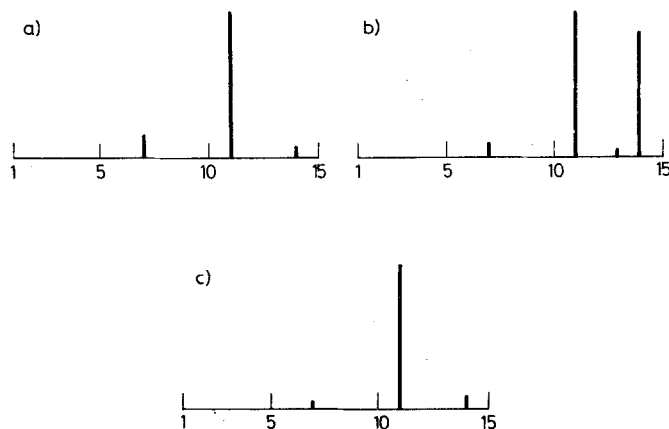


Fig. 3 The spectra obtained by isothermal data with: A) $C_1=0.7$, $C_2=0.3$; B) $C_1=0.5$, $C_2=0.5$; C) $C_1=0.3$, $C_2=0.7$

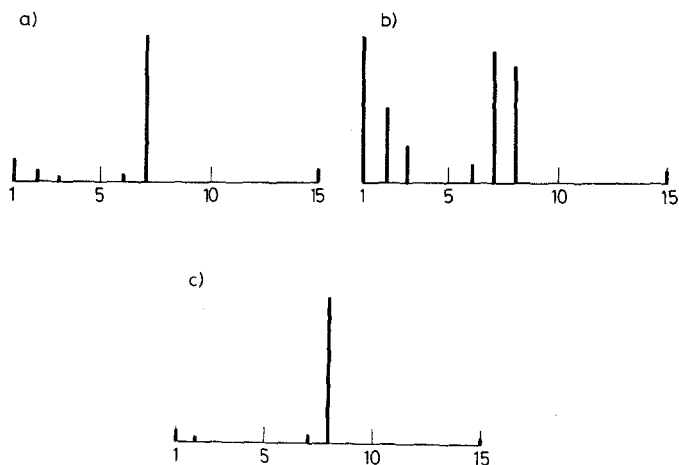


Fig. 4 The spectra obtained by non-isothermal data with: A) $C_1=0.7$, $C_2=0.3$; B) $C_1=0.5$, $C_2=0.5$; C) $C_1=0.3$, $C_2=0.7$

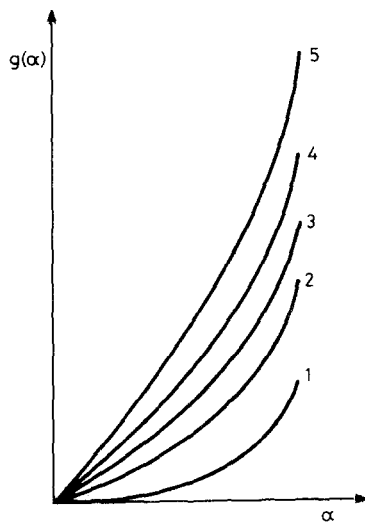


Fig. 5 Base functions (1, 5) and linear combinations: 2. $C_1=0.3$, $C_2=0.7$; 3. $C_1=0.5$, $C_2=0.5$; 4. $C_1=0.7$, $C_2=0.3$

nonisothermal case. The explanation is that the linear combination as a kinetic function description determines its intermediate character relative to the base functions (Fig. 5). Hence, the strongest spectrum lines correspond to those kinetic functions which give the best description of the linear combination, i.e. those which are most probable in this case.

Random error effect on the spectrum form

As the spectra are calculated at prescribed decomposition degrees (0.1, 0.2, . . . , 0.9), it was assumed that only temperature (time in the isothermal case) contains a random normally distributed error. Considering these assumptions, the quantities containing an experimental error conform with [7]:

$$T_j = T_j^0 + \sigma x_j \quad (7)$$

where T_j^0 is the model temperature (time), σ is the prescribed r.m.s. deviation, and x_j is the random normally distributed number. The values of x_j can easily be obtained using the generator of uniformly distributed random numbers R_i [7]:

$$x = \frac{\sum_{i=1}^n R_i - \frac{n}{2}}{\sqrt{\frac{n}{2}}} \quad (8)$$

As noted in [7], at $n = 12$ formula (8) yields satisfactory values of random numbers. We have used the higher value $n = 48$, as with increasing n distribution (8) asymptotically approaches the normal one in accordance with the central limit theorem [8].

In Fig. 6, the spectra based on nonisothermal data exemplify the effects of random errors on the form of the spectra for $C_1 = 0.7$ and $C_2 = 0.3$. It can be seen that, with increasing error σ , the spectra change essentially. We have found, however, that at a prescribed σ and various combinations of random deviations for

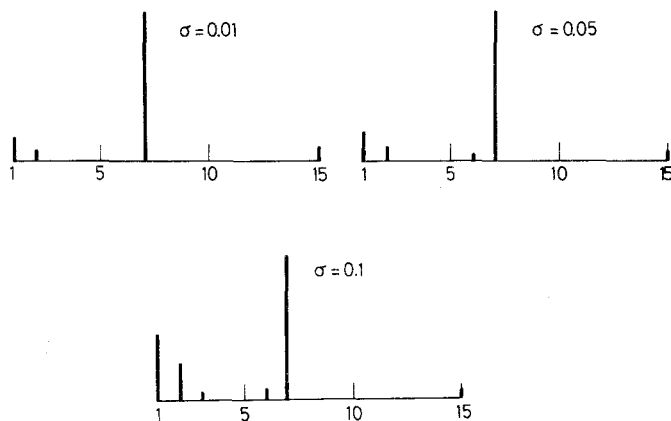


Fig. 6 Influence of random error level on the spectra obtained by non-isothermal data for $C_1 = 0.7$, $C_2 = 0.3$

T_j^0 , the spectrum form for constant C_1 and C_2 is preserved (the error does not exceed 5% of the line strength).

Accordingly, it is clear that changes in the form of the spectrum with varying experimental conditions may be due to two reasons: the changing character of the process, or the changing level of the experimental error σ . In this case, while the changes in the heating rate (temperature) alter the form of the spectrum, which, being changed, remains constant at some heating rates (temperature), the changes in the spectrum are due to variation in the process behaviour. If no regular change is observed in the form of the spectrum with varying experimental conditions, the change is random (i.e. caused by uncontrollable reasons) and the results of measurement for such experimental conditions should be omitted from the calculations.

Conclusion

The method suggests a generalized description of the process using a probability spectrum of kinetic functions. This spectrum is shown to possess invariance relative to both experimental errors (at a constant level of the error σ) and experimental conditions (temperature for isothermal conditions and heating rate for nonisothermal ones). Since measurements for one and the same group of samples on an instrument in a certain precision class contain an experimental error of one and the same level σ , a method may be suggested to control changes in the process under either isothermal or nonisothermal conditions.

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Zusammenfassung — Eine Methode, basierend auf dem Komplementärprinzip, zur allgemeinen kinetischen Beschreibung von Festphasenvorgängen wird beschrieben. Diese ermöglicht, Spektren als diskrete Verteilung der Wahrscheinlichkeit der Beschreibung von Vorgängen als Ausdrücke kinetischer

Funktionen in Übereinstimmung mit deren Ordnungszahlen auszudrücken. Die erhaltenen Spektren ermöglichen es, mit Veränderungen der Vorgangsbedingungen in Verbindung stehenden Veränderungen im Verhalten von Festphasenvorgängen zu verfolgen.

Резюме — Предложен метод обобщенного кинетического описания твердофазных процессов, основанного на принципе дополнителности. Метод позволяет получить спектры, представляющие собой дискретное распределение вероятности описания процесса с помощью отдельных кинетических функций по их порядковым номерам. Полученные спектры позволяют контролировать изменение характера твердофазного процесса при изменении условий его протекания.