

SOME ASPECTS OF MATHEMATICAL STATISTICS AS APPLIED TO NONISOTHERMAL KINETICS

Part IV. Methodological Aspects

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The problems of the adequate description of a heterogeneous process are considered by using the methodology of formal nonisothermal kinetics. It is shown that the contradiction between the certainty of the process mechanism and the uncertainty in its description cannot be solved within the traditional methodology of solving the inverse kinetic problem. As an alternative to the traditional methodology based on the principle of unambiguous description, the methodology based on the complementarity principle is suggested. The latter is advantageous to obtain information on the process from the set of its ambiguous solutions.

The diversity of heterogeneous processes and their complexity give rise to the majority of specific methods of studying these processes, such as experimental methods, processing of experimental data, and calculation of kinetic parameters. The available methods raise the problems of choosing the most efficient of them and of their optimum interrelation. These problems can be solved only within the framework of a certain methodology, which allows one logically to combine different methods in one system so as effectively to achieve a particular aim of the study. The development of the methodology of nonisothermal kinetics implies the most general understanding of both the goals of the nonisothermal kinetics and the problems of their achievement. Such an understanding is concerned in the Šestak paper [1], which considers some diverse and general problems of nonisothermal kinetics.

In fact, the methodology of nonisothermal kinetics should serve its main purpose, namely the study of the regularities and the mechanism of heterogeneous processes under nonisothermal conditions. As concerns formal nonisothermal kinetics, this is one of the approaches to the study of heterogeneous processes. The

specificities of the method are determined by its aim of obtaining information on the regularities of the process, using its adequate formal description. This aim can be achieved through the creation of a formal description which can adequately reveal the essence of the process. This is the idea which underlies the methodology of formal nonisothermal kinetics and thus specifies the major problem of this methodology: to choose and combine in a system those methods of studying nonisothermal processes which would provide the most informative and adequate description of a process.

In view of this methodological problem, our study is aimed at a consideration of some methods and the possibility of their combination in one system. In our view, this would secure the most adequate formal description of nonisothermal processes, and hence would allow achievement of the above aim of formal nonisothermal kinetics.

It is worth noting that the degree of adequacy of a formal description can be increased, first, by improving the proper formal methods (methods of calculating kinetic parameters and of processing experimental data), some of which are noted in [2] and discussed below. Second, it is possible by using more widely those nonformal (experimental) methods that permit formalization within the fundamental equation of nonisothermal kinetics (1):

$$\frac{d\alpha}{dT} = \frac{A}{q} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

or, in other words, using the conventional methods of nonisothermal kinetics. The latter possibility, considered in the part dealing with the methods of invariant kinetic parameters, may be combined with the former one, thereby increasing the adequacy of the formal description, which will finally decrease its uncertainty.

Formal methods

We shall note three major theoretical problems related to Eq. (1):

- (i) the problem of reading out kinetic curves;
- (ii) the problem of calculating kinetic parameters;
- (iii) the problem of the adequacy of kinetic functions.

Let us now consider each of these problems in more detail, in view of the methods which allow their solution.

(i) Two problems should be noted here: first, concerning the number of points necessary for an adequate description of the kinetic curve; second, the connection of the readout frequency and information content of different segments of the kinetic curve. The first problem is usually solved using the Nyquist criterion [3] or

the Kotelnikov theorem [4]. Both of these enable one to determine the minimum number of required equidistant readouts. A number of points below the prescribed number does not allow an adequate description of the kinetic curve, i.e. without losing the information on the real process which is contained in the entire kinetic curve. Thus, it is noted in [2] that an adequate description of the kinetic curve requires about 10^2 points. Both methods [3, 4] have been stated to give the number of equidistant readouts following from the equidistant property of the underlying Fourier transform. However, Shannon [5] emphasizes that the number of readouts may also be applied when the latter are not equidistant. Further, the use of nonequidistant readouts allows one to choose those points on the kinetic curve which involve the greatest amount of information about the process, and thus permit its more informative description.

(ii) This problem, we think, has two main aspects: one is associated with the linearization effect on the kinetic parameters, and the other with the stability of the calculation method to the scatter in the experimental data. As concerns linearization, it is a very convenient, though not a very correct mathematical method. Linearization gives rise to an effect of a "regression shift to the past" [6], i.e. linearized form (1) gives the values of the kinetic parameters describing mainly the initial sections of the kinetic curves. It is evident that, by introducing additional relations absent from Eq. (1), the linearization method makes the formal kinetic analysis more intricate and distorts the description of the real processes under study. Nonlinearized form (1) allows a more adequate description of the processes from the formal viewpoint and is therefore to be preferred. As for the stability of the computational method, we primarily mean the stability of the least squares method to the scatter in the experimental data. It is known that the estimates of the least squares method (kinetic parameters) are optimum only provided the hypothesis on normal error distribution is fulfilled. However, this hypothesis is extremely rigid under real conditions [7], and in particular the scatter in the experimental data is encountered in practice more often than follows from Gaussian distribution. Therefore, the available procedure to obtain robust estimates [8, 9] presents an alternative to the least squares method and makes it possible to eliminate those data which are accidental in their essence and characterize the external conditions of the process rather than the process itself.

In connection with problem (ii), let us dwell in short on the reasonability of a further increase of the number of methods to calculate kinetic parameters. This increase is only appropriate when the method is based on a new mathematical model different from (1). If the methods are based on Eq. (1), they contain the same idealized notion on the chemical process underlying (1). The essence of this notion can be expressed by the following pre-requisites. First, the energy barrier must be overcome for the reaction to proceed [1]. Second, the reaction rate is proportional

to the number of active sites in the reactive zone. Hence, none of the methods of calculating kinetic parameters based on (1) can give more information towards an understanding of the essence of the real processes than (1), as they do not contain anything in excess of (1). The only excuse for an increasing number of calculation methods based on (1) is that different methods differ in their accuracy and in the convenience of their application, depending on the aim and experimental method of its achievement.

(iii) The problem of the adequacy of the kinetic functions for real heterogeneous processes turns out to be one of the most difficult in formal kinetics. It is evident that the use of a larger number of kinetic functions in formal kinetic analysis is unreasonable. This is evidenced by the fact that some kinetic functions that are different in mathematical form give practically very close values of the kinetic parameters, i.e. they actually characterize very similar model processes, but describe them in a different mathematical form. This may be exemplified by the kinetic functions of diffusion processes which, having a different mathematical form, as a rule give the values of kinetic parameters differing within an error. Perhaps the diversity of kinetic functions results at least from the diversity of the processes they describe (besides diffusion, Delmon [10] emphasizes only two major groups of processes affecting the total kinetics: nucleation and boundary development), rather than from the great relative independence of mathematical approaches which give a set of the means to formalize the processes of one type.

Thus, it is clear that a combination of the available kinetic functions into classes [11] corresponding to the processes of a certain type, and therefore having a different physical essence, will enable one to choose such a class more uniquely as compared to the choice of individual kinetic functions which often differ only in the mathematical form of the realization of one and the same physical meaning.

Nonformal (experimental) methods

Two aspects may be indicated which promote the achievement of the above aim of formal nonisothermal kinetics using nonformal methods. First, improvement of the nonformal methods proper; second, improvement of the formal description due to nonformal methods. As concerns the first aspect, it by no means touches upon the formal description of processes and includes three major problems:

(i) the problem of increasing the accuracy of experimental measurements methods;

(ii) the problem of providing 'ideal' experimental conditions;

(iii) the problem of reproducible properties of the test object.

(i) As noted above, those methods are meant here which allow formalization

within Eq. (1), i.e. TG, DTA, volumetry, etc. It is clear that the increasing accuracy of these methods increases the amount of signal information on the real process itself against accidental deviations due to foreign reasons. Nevertheless, however, high the measurement accuracy, it is impossible to exclude accidental deviations completely. Thus, the robust calculation methods mentioned in the previous part always remain actual.

(ii) It is evident that, even if we possess the most perfect methods of formal description and the most exact measurement methods, it is impossible to obtain information which is not included in the experimental data. Therefore, the problem arises of providing experimental conditions which would permit study of the process in the most 'pure' form. This necessity results directly from the assumptions underlying the formal methods describing heterogeneous processes, such as the monodispersity of an object, the uniform temperature distribution inside it, the absence of a back-reaction, and so on. These 'ideal' conditions are achieved using a set of methods to prepare the test objects [12], such as extraction of the fractions of definite dispersion, heat dilution, small samples, etc. Methods are also applied which prescribe the external experimental conditions: the use of low pressures, continuous reactors, temperature programs which allow the process to be studied under nonequilibrium conditions, etc.

It should be noted, however, that even the creation of extremely 'ideal' conditions (monocrystal decomposition in vacuum) does not permit extraction of the chemical stage of the heterogeneous process in a 'pure' form, as it is already a macrokinetic one at the microscopic level [13]. This essentially restricts the methods designed to create 'ideal' experimental conditions, whose achievement with regard to a real solid structure is a more difficult problem than (i).

(iii) It is well known that solids having similar atomic compositions, but different pre-histories, behave differently in chemical processes. The ensuing problem (iii) is mainly solved by using nonformal (experimental) methods which reduce to standardizing the conditions of obtaining and processing the test object noted in [10]. However, in spite of such standardization, the "production of a series of samples with identical properties can always be regarded as a success" [10]. This results from the fact that it is impossible in principle to keep constant the very great number of factors required to provide the reproducibility of the properties. As concerns the problem solution by formal means, this is still no more than a tempting prospect.

(iv) It should be noted that the improvement of the formal description by using nonformal methods can be implemented by extending the variety of the experimental conditions and methods. The extension of the variety of the methods and conditions applied for the investigation of heterogeneous nonisothermal processes increases the number of possible formal process mechanisms and extends

the range of kinetic parameters, while it also allows elucidation of the stable, unchanging regions both of formal mechanisms and of kinetic parameters. Such stable (invariant) regions are revealed at the stage of synthesizing the total formal picture of the process on the basis of its individual aspects, found under different experimental conditions by means of different experimental methods. Such a picture can be obtained within the method of invariant kinetic parameters.

This method is suggested in [14]. In contrast to other approaches, it is a method in a wider sense and acts as a methodological principle to increase the adequacy of the formal description of the process and the reliability of the kinetic parameters when conventional methods are used. In this case, use is made of the traditional methods of nonisothermal kinetics and a standard set of formal models of heterogeneous processes united by the compensation effect. The latter is a strongly elongated elliptical confidence region in the space of the kinetic parameters. Such a formal approach permits retention of the essence of the formal description of the process to a greater extent as compared to the description by means of individual formal models. Due to the variation of the experimental conditions (for example, of the heating rate), a set of intersecting confidence regions with a common intersection region is formed. It is this intersection region which reflects in the kinetic parameter space of the invariant (stable to the variations of experimental conditions) essence of the process. As the intersection region is smaller than the individual confidence regions, the ambiguity of the solution of the inverse nonisothermal kinetics problem decreases, and hence the adequacy of the formal description increases. Therefore, we think it most promising to develop formal methods and especially those which allow the improvement of a formal description, by using a wide spectrum of both formal kinetic models and nonformal (experimental) conditions. Naturally, the increasing adequacy of the formal description inevitably increases the bulk of experiments and calculations, However, at the modern level of development of experimental and computing techniques, this result does not cost too much.

Complementarity of kinetic functions

It is specific of the solution of the inverse nonisothermal kinetics problem that the kinetic functions do not represent the proper solution of Eq. (1), i.e. they were obtained independently. In this connection the question arises of whether it is possible in principle to obtain a single solution to (1) using the conventional set of kinetic functions. Multiple unsuccessful (if the problem solution was mathematically correct) attempts to choose 'the best' kinetic function may give a convincing answer. The reasons for these failures are presumably to be sought in the very nature of the kinetic functions being a formal mathematical description of idealized

processes. This is why any kinetic function describes only some features of the real heterogeneous process, which are inherent in the corresponding idealized process. As a result, because of the inevitable incompleteness of describing a real process in terms of individual kinetic functions, there is always a certain set of functions which allow it to be described. The possibility of a formal-and-mathematical description of the process via kinetic functions being admitted in principle, it must also be admitted for each of the functions of a certain set. This amounts to the admission of the equal ability of the functions of a certain set to contain certain, but not equivalent (if the functions belong to different idealized processes) information about the process. Hence, the contradiction immediately follows between the certainty of the process mechanism and the uncertainty in its formal-and-mathematical description. In order to solve these contradictions, methods are required to extract information about the process from the contradictory information provided by the kinetic functions which constitute the set of solutions to the inverse kinetic problem.

The traditional methodology of solving the inverse kinetic problem by *analysing* the real process (i.e. by dividing it into individual aspects corresponding to kinetic functions) fails to provide the methods required to solve the above contradiction. This circumstance results from the principle of unambiguous description which underlies the traditional methodology and requires that the 'best' kinetic function be sought. This is why, in the framework of the traditional methodology, the functions constituting the set of solutions to the inverse kinetic problem are 'competing', and their 'discrimination' is the major problem.

The necessity of solving this contradiction requires that the alternative to the traditional methodology be sought. We think that this can be any approach to the solution of the inverse kinetic problem which assumes *the synthesis* of a more sense-bearing formal picture of the process from the information about its individual features provided by 'competing' kinetic functions. Such a synthesis, in essence, is one of the possible forms of the synthetic approach, the necessity of which in studies of the kinetics of heterogeneous processes was pointed out by Delmon [10].

The principle of complementarity, which allows the description to be considered as the reflection of different, but equally important features of the process, is a formal and logical basis of the synthesis of the integral process picture from a set of its contradictory descriptions. Accordingly, the principle of complementarity provides a unique possibility of synthesizing the united picture of the process based on inconsistent (within the traditional methodology) descriptions.

The general epistemological nature of the principle of complementarity [17, 18] allows it to be applied to the set of kinetic functions constituting the variety of solutions of the inverse kinetic problem, and thus being contradictory descriptions of one and the same process. In view of this principle, the kinetic functions which

formally describe the process equally well should be considered as complementary rather than competing. Such an approach to the ambiguity of the inverse kinetics problem solution ensures that a great amount of information can be gained (provided the entire information provided by the complementary kinetic functions is used) as compared to the traditional methods, which use the information presented by a single kinetic function. The high information content of the approach based on the complementarity of the kinetic functions yields a more unambiguous description of the process. The latter implies a more exact estimation of the kinetic parameters (within an error, an estimation of the kinetic parameters coinciding with their isothermal values) and assignment of the process to a certain class. A sufficient number of particular examples which support the above advantages of the complementarity-based approach can be found elsewhere [11, 14–16].

The use of the complementarity principle rather than an unambiguous description is equivalent to the use of the nontraditional approach we suggest, instead of the traditional methodology of solving the inverse kinetic problem. Particular cases of the suggested nontraditional methodology include the unified approach to the analysis of kinetic functions [11] and the method of invariant kinetic parameters [14]. Both approaches describe the process by using such synthetic notions as the class of kinetic functions [11] or the apparent compensation effect [14], the essence of which can only be understood on the basis of the complementarity principle. Further, in order to obtain invariant kinetic parameters [14] of the process, the compensation effects for different experimental conditions should be considered complementary to each other (i.e. as different descriptions of one and the same process under appropriate experimental conditions). This is the only case, when the invariant kinetic parameters corresponding to the region of intersecting compensation effects may be regarded as the parameters of a certain process, and hence as having the sense of invariants.

The above partial cases of applying nontraditional methodology [11, 14] are the first attempts, and therefore have some shortcomings. In particular, the method of invariant kinetic parameters does not greatly decrease the uncertainty of the formal description in those cases when the angular coefficients of the compensation relation change slightly with variation of the experimental conditions. The development of this method requires the improvement of the specific statistic analysis of the interrelated correlations whose fundamentals are presented in [19–21].

As concerns the use of the unified approach for the analysis of the kinetic functions [11] in solving the inverse kinetic problem, this allows the unique assignment of the process under study to a certain class (diffusion, nucleation, power law, reaction order). However, the exact values of the kinetic parameters

remain undecided, since it is necessary to choose only a single function inside a class, which would contradict the complementarity principle underlying the suggested nontraditional methodology. Therefore, the kinetic parameters within a class vary as the kinetic parameters corresponding to the functions of this class which give a statistically equivalent description of the process.

Conclusion

Accordingly, the critical analysis of particular approaches on the basis of nontraditional methodology shows that they allow one to decrease the uncertainty in the formal description, but do not exclude it completely. The explanation may be the following. In accordance with the adopted classification of the methods increasing the adequacy of the formal description into formal and non-formal (experimental), two kinds of uncertainties can logically be distinguished. Formal uncertainty results from imperfect formal description methods. Non-formal (experimental) uncertainty stems either from the specificity of the process or from imperfect experimental methods. It is evident that the approaches we suggest permit only formal uncertainty to be restricted (as far as this is possible in principle). Therefore, the main contribution to the residual uncertainty in the formal description of processes within nontraditional methodology is of a non-formal nature. Thus, the residual uncertainty in the method of invariant kinetic parameters, which results from small changes of the angular coefficients in compensational dependences with variation of the experimental conditions, is determined by the specificities of the processes and by restricted variation of the experimental conditions. The elimination of non-formal uncertainty is beyond the framework of formal kinetics, which only generalizes the experimental data in terms of definite model representations. This can be achieved by using special sophisticated experimental methods of local study of the reaction zone, which are now being developed within the isothermal kinetics to study the reaction mechanism. Their application and improvement involve great difficulties, often of principle.

Thus, the problem arises of choosing either the last approach, which promises a comprehensive knowledge of the elementary stages of the process, or an approach similar to the one discussed in the paper, which will provide a generalized and schematic picture of the process. It should be noted that in many practical cases the schematic picture may turn out to be not only sufficient, but also preferable. This is because the transition from a comprehensive knowledge of the regularities of the elementary process stages to a knowledge of the regularities of the entire process in a real object under real conditions is by no means less difficult than the reverse

transition. The extension of the extrapolation possibilities of the process description for the experimental conditions using the class of kinetic functions obtained in accord with [11] and the kinetic parameters obtained in accord with [14] is evidence for this. However, the final choice of the approach should be made by the researcher and depends on the particular aims of the investigation.

References

- 1 J. Šestak, *J. Thermal Anal.*, 16 (1979) 503.
- 2 J. Šestak, *Thermophysical Properties of Solids*, Academic Prague, Prague, 1984.
- 3 H. Nyquist, *AIEE Trans.*, 47 (1928) 617.
- 4 G. A. Korn and T. M. Korn, *Mathematical Handbook*, McGraw-Hill, 1968.
- 5 C. Shannon, *Proc. IRE*, 37 (1949) 10.
- 6 E. Z. Demidenko, *Linear and Nonlinear Regression*, Moskva, *Finansy i Statistika*, 1981 (in Russian).
- 7 J. M. Tukey, *Ann. Math. Stat.* 33 (1966) 1.
- 8 P. Huber, *Robust Statistics*, J. Wiley, N.Y., 1981.
- 9 *Robustness in Statistics*, Academic Press, N.Y., 1979.
- 10 B. Delmon, *Introduction à la Cinétique Hétérogène*, Paris, Editions Technique, 1969.
- 11 S. V. Vyazovkin and A. I. Lesnikovich, *J. Thermal Anal.*, 32 (1987) 249.
- 12 V. A. Logvinenko, *Thermal Analysis of Coordination Compounds and Clathrates*, Novosibirsk, Nauka, 1982 (in Russian).
- 13 N. Z. Lyakhov, *Izv. SO AN SSSR, Ser. Khim. Nauki*, 2 (1985) 3.
- 14 A. I. Lesnikovich and S. V. Levchik, *J. Thermal Anal.*, 27 (1983) 89.
- 15 A. I. Lesnikovich and S. V. Levchik, *Thermochim. Acta*, 77 (1984) 357.
- 16 A. I. Lesnikovich and S. V. Levchik, *J. Propulsion and Power*, 1 (1985) 311.
- 17 H. Primas, *Chemistry, Quantum Mechanics and Reductionism*, Berlin, Springer, 1981.
- 18 H. Primas, *Chimia* 36 (1982) 293.
- 19 V. I. Shimulis, *Kinetika i Kataliz*, 24 (1983) 715.
- 20 O. Exner, in: *Progress in Physical Organic Chemistry*, Vol. 10, N.Y., J. Wiley, 1973, p. 411.
- 21 R. R. Krug, W. G. Hunter and R. A. Grieger-Block, in: *Chemometrics; Theory and Appl. Symp. 172nd Meet. Amer. Chem. Soc., S.F. Calif., 1976, Washington, D.C. (1977) 192.*

Zusammenfassung — Die Probleme einer adäquaten Beschreibung heterogener Prozesse werden unter Verwendung der Methodologie der nicht-isothermen Kinetik erörtert. Es wird gezeigt, daß der Widerspruch zwischen der Sicherheit des Prozeßmechanismus und der Unsicherheit in dessen Beschreibung nicht im Rahmen der traditionellen Methodologie zur Lösung inverser kinetischer Probleme gelöst werden kann. Als Alternative zur traditionellen, auf dem Prinzip der eindeutigen Beschreibung beruhenden Methodologie wird eine auf dem Komplementärprinzip basierende vorgeschlagen, die geeignet ist, Informationen über den Prozeß aus einer Reihe von nicht eindeutigen Lösungen zu liefern.

Резюме — С точки зрения методологии формальной неизотермической кинетики рассматриваются проблемы адекватного описания гетерогенного процесса. Отмечается, что противоречие между определенностью механизма процесса и неопределенностью его описания не может быть разрешено в рамках традиционной методологии решения обратной кинетической задачи. В качестве альтернативы традиционной методологии, основанной на принципе однозначного описания, предлагается методология, основанная на принципе дополтельности. Преимущества последней состоит в возможности извлечения информации о процессе из совокупности его неоднозначных описаний.