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ON THE METHODS OF SOLVING THE INVERSE PROBLEM OF SOLID-PHASE REACTION KINETICS

I. Methods based on discrimination

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This review deals with the choice of a method of solving the inverse kinetic problem (IKP) which would provide the most definite description of the process under conditions of ambiguity. Two fundamentally different methodologies are possible for the IKP solution: one is based on the principle of unambiguous description (discrimination), while the other relies upon the complementarity principle (generalized descriptions). Specific IKP solution methods have been classified, the methodological differences being taken into account. In the first part of this review, general and special limitations in discrimination of formal models have been analysed.

The IKP is one of the most intricate problems in the formal kinetics of solid-phase reactions (particularly in the nonisothermal case). A researcher wishing to apply the techniques and instruments of thermal analysis is often completely nonplussed by the vast and increasing diversity of approaches to the problem. A further improvement of the IKP solution classification, and systematization of the available approaches from different standpoints, may be very helpful in such a situation. We consider it useful to divide the IKP solution methods into groups possessing common properties in respect of the information that may be obtained by solving this problem. The review seeks to analyse IKP solutions with the above points in view.

The IKP is a particular case of a wide class of inverse system analysis problems solved in order to find an equation that would describe the system behaviour in terms of the present input and output signals [1]. All inverse problems are regarded as incorrect ones [2], as in the general case their solution is ambiguous.

The IKP, whose solution is the formal model of a process and its effective kinetic parameters (activation energy and pre-exponent), is characterized by two kinds of ambiguity [3–5]. The ambiguity of the first kind stems from the situation when only

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a limited number of kinetic constants can be determined via experimental data [3–6]. When attempts are made to estimate a higher number of kinetic constants, the latter lose their independence, and, as result, their numerical values lose physical meaning. The overcoming of the first kind of ambiguity through an analysis of Jacobi matrices is dwelt on in [4–6]. This approach for solid-phase kinetics is discussed in [7]. The ambiguity of the second kind implies that a set of experimental data can be described successfully by different sets of formal models and kinetic constants [3–5]. It is worth noting that, unlike the ambiguity of the first kind, which can be eliminated completely, the ambiguity of the second kind can only be reduced to some extent [8]. It is precisely this reduction of the ambiguity that is thought to be the main goal of any IKP solution method. Differentiation should be made here between the "IKP solution method" and the "method of calculating kinetic parameters". The kinetic parameters of a process can obviously be calculated, provided certain assumptions are made concerning its formal model. For example, the assumption that the kinetic parameters should be calculated following the formal model which offers the best description of the experimental data underlies the statistical approach to the solution. A whole set of kinetic parameter calculation methods, e.g. the Borchardt–Daniels [9], Šesták–Berggren [10] methods, etc., can in turn be used within the framework of the statistical method.

It should be noted that the classification of IKP solution techniques suggested in this manuscript also makes it possible to combine the kinetic parameter calculation methods as certain groups possessing common properties with respect to the IKP solution. In fact, it classifies the kinetic parameter calculation methods themselves. The conventional classification [11–15] of the kinetic parameter calculation methods by dividing them into differential and integral ones, relying on the experimental data used, offers no inference as the extent to which the calculated parameters are a reasonable IKP solution.

Further, our work is far from being a comprehensive review of the kinetic parameter calculation methods (these can be found elsewhere [11–15]). We shall use them for purposes of illustration. At the same time, the paper complements the above reviews with new studies from the eighties and the calculation methods that have not received adequate attention. First of all, they include the isoconversional [16] and similar calculation methods. These methods are of fundamental importance for our classification based on the methodological principles suggested in [8] and considered briefly below.

Classification principles

It is shown in [8] that there are two basically different approaches to the IKP solution or, in other words, two ways to reduce its ambiguity. The first, traditional way (analysis) is used to discriminate the competing formal models of the processes in order to choose the only "best" one. This way relies on the principle of unambiguous description. The second, nontraditional way (synthesis) is used to derive generalized (synthetic) descriptions from a set of competing models. It is based on the complementarity principle. Precisely these two, the complementarity principle and principle of unambiguous description, form the basis of the proposed classification. The further discussion will follow the short classification presented in Fig. 1.

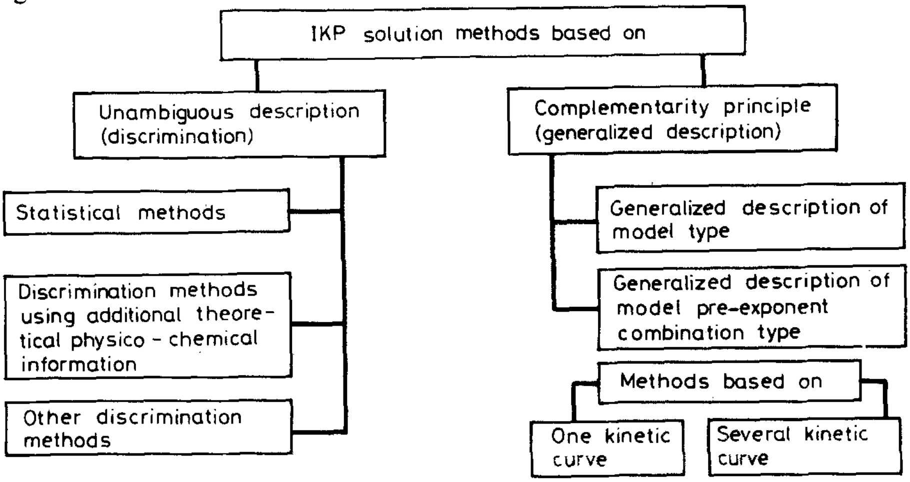

Fig. 1 The classification of the IKP solution methods

IKP solution methods based on unambiguous description (discrimination)

These methods reduce the ambiguity of the IKP solution by discriminating the competing models in order to choose the only "best" one. Any discrimination relies upon additional information which is external with respect to a specific experiment as it is obtained from outside. Generally, this is information about the nature of the process or the properties of the inverse problem solution. In the overwhelming majority of cases, the IKP is solved by using statistical methods of discrimination.

Statistical methods of discrimination

For discrimination, the methods of this group use additional information on the kind of distribution of random values. The latter include, for instance, such statistical characteristics as the correlation coefficient and the residual sum of squares calculated by fitting the parameters of Eq. (1)

$$d\alpha/dt = A \exp(-E/RT) f(\alpha) \qquad (1)$$

where $d\alpha/dt$ is the process rate, A and E are the kinetic parameters (pre-exponent and activation energy, respectively), R is the gas constant, T is the absolute temperature, $f(\alpha)$ is the formal model of a process and α is the transformation degree. As the IKP solution, one formal model with corresponding parameters is chosen. It is consistent with an extreme value of the statistical characteristic used for the IKP solution. In discriminating the IKP solutions, it is mandatory to test statistical characteristics for homogeneity. An unambiguous choice of the IKP solution model is only possible within a certain confidence interval when the extreme value of the statistical characteristic and its closest value are inhomogeneous. Different aspects of statistical tests as applied to model discrimination are dwelt on in [18–21].

Among the kinetic parameter calculation methods most widely used [22] is Zsakó's method [23]. These methods apply a statistical characteristic, such as the standard deviation of the experimental temperature integral $g(\alpha)$ from the theoretical one ($p(E/RT)$): $B_i = \log g(\alpha_i) - \log p(E/RT_i)$. As noted in [20], the ratio of the squared standard deviations δ calculated in Zsakó's method

$$\delta = \sqrt{\sum_i (B_i - \bar{B})^2 / r}$$

($\bar{B}$ being the average of all B_i and r being the number of points) obeys Fisher's distribution [17]. The latter offers the F-test for discrimination of the $g(\alpha)$ process models. Thus, the use of the F-test to verify the homogeneity of the standard deviations cited in [23] (complex 1) has exhibited their homogeneity for three $(1-\alpha)^n$ models at $n = 0$, 1 and 2. Hence, the choice of the model with $n = 1$ [23] for the minimum standard deviation is statistically unjustified. Statistical tests are not used either in processing experimental data by Zsakó's method in other references [24, 28] or in its computer version [26]. It should be noted that the use of experimental data [26] can easily show that the F-test offers an unambiguous choice of the model $(1-\alpha)^n$ with the set $n = 0$, 0.5, 0.67 and 1. This does not imply, however, that in this case the unambiguous choice would have been possible if a much wider spectrum of formal models different from $(1-\alpha)^n$ had been used.

The statistical methods of IKP solution using a wide set of formal models were applied, for instance, in [19, 27–32]. In [27], the results on the thermogravimetric decomposition of a complex compound were interpreted with the aid of the Šatava method [33]. The correlation coefficient, whose maximum turned out to be equal for five Avrami–Erofeev models with different power exponents, was used as a statistical characteristic for discrimination. The activation energies consistent with these models ranged from 50 to 342 kJ/mol. In [28], the results of the thermogravimetric decomposition of citric acid were processed by using the Reich–Stivala method [29], implementing statistical discrimination on the basis of the standard error proved to be minimum for the diffusional Junder model. However, more than 1000 experimental points are required to discriminate the Ginstling–Brounstein model, closest to it in the standard deviation value, within 95% probability.

Various kinetic parameter calculation methods are compared theoretically in [30] with the correlation coefficient and standard error as a discrimination criterion. The maximum value of the former and the minimum of the latter are found to be consistent with different models. This fact is one of the reasons why a single model should not be chosen via an extreme value of some statistical characteristic. It should be noted [30] that, even for the theoretical data simulated according to the first-order reaction and Avrami–Erofeev (power exponent 2/3) equations, the integral methods of kinetic parameter calculation suggested by Boy and Bohme [34] and Coats and Redfern [35] do not allow one to discriminate between the Avrami–Erofeev (power exponents 2/3 and 1/2) and first-order reaction models in terms of the statistical characteristics used in [30]. The kinetic parameters corresponding to the above three models differ by a factor of 3–4 times, depending on the calculation procedure. It has also been found [30] that, following the Boy–Bohme method, the experimental data on kaolinite decomposition are described best of all by the standard error by the Avrami–Erofeev model (power exponent 1/2). About 50 points are required for unambiguous discrimination of the competing second-order reaction model. The activation energies calculated with these competing models differ by a factor of about as much as 3 times.

The statistical tests in [31, 32] have reduced the number of competing models rather than offered a certain formal process mechanism. It is worth noting here that the isothermal experiment regarded as being more accurate does not allow one to make an unambiguous choice of a model [27, 32, 36].

The statistical IKP solution methods often apply to a purely mechanistic approach based on the adjustable parameter model (reaction order or Avrami–Erofeev model). In this case, the inverse problem solution is reduced to the finding of the adjustable parameter consistent with the extreme value of some statistical characteristic. In the adjustable parameter case, it is most convenient to reduce Eq. (1) to its linear form through a logarithmic transformation. Then, the adjustable parameter can easily be found together with the kinetic parameter by using multi-dimensional linear regression [37, 38]. This is the way in which the kinetic parameters and the reaction order are determined by using the standard software of the Mettler TA 3000 analyzer [39]. The estimates so obtained comply with the minimum residual sum of squares [17]. The order of reaction in [40, 41] was chosen in terms of the highest linearity, with the linear correlation coefficient used [42–44] as its numerical characteristic for the IKP solution. The BASIC program text in [44] allows the order of reaction to be calculated via the maximum correlation coefficient. Fitting of the adjustable parameters for both models (reaction order and Avrami–Erofeev models) is dwelt upon in [45–47], assuming the correlation coefficient and the standard deviation at one time to be statistical characteristics. The adjustable parameters obtained in this way in the above models often fail to be interpreted on physical grounds. Thus, in [46] the isothermal dehydration of magnesium oxalate can be appropriately described by both the reaction order ($n = 1.56$) and Avrami–Erofeev ($m = 2.36$) models. In this instance, the activation energy values are practically equal (the latter specificity of isothermal kinetics [48] will be discussed below). Similarly, in [47] barium oxalate dehydration is equally well described by the reaction order and Avrami–Erofeev models.

The single adjustable parameter model can hardly be considered to be universal, and this is the main reason why it should not be widely used in the IKP solution. However, if such a model could adequately describe the kinetic curve geometry, it would be possible to use it [49] and to derive practically valuable information [50]. The great errors in the kinetic parameters estimated via the widely-used [22] Freeman–Carroll method [51], based on the $(1-\alpha)^n$ model, provide evidence, among others, against the application of the reaction order model. Modelling of the kinetic curves in accordance with various found mechanisms and further calculations of the kinetic parameters via the Freeman–Carroll method show [52] that the activation energy error may constitute 50% of the true value. However, the experimental dependence is linearized here in corresponding coordinates with a correlation coefficient of more than 0.99999 [52]. The inapplicability of the Freeman–Carroll method was also emphasized in [53]. The modification of this method to increase its accuracy is suggested in [54]. Along with the Freeman–Carroll method, reference [55] deals with the Horowitz–Metzger method for the calculation of kinetic parameters on the basis of the reaction order model. Both methods are shown to result in great errors when applied to process model data. To be specific, the activation energy values may be as much as 10 times different from the model value [55]. Hence, the applicability and universality of the reaction order model are always debatable [56, 57].

The linearity of the experimental data in the coordinates of the Kissinger equation, derived on the assumption that it is feasible to describe a process in terms of the reaction order model, provides evidence in [58] of the applicability of the equation $(1-\alpha)^n$ for the description of solid-phase processes. Such evidence, however, is restricted by the fact that the range of applicability of the Kissinger method, as will be shown below, does not only include the processes governed by the reaction order model. The authors of [60] offer a more reliable verification of the reaction order model, which is advised as a reliability test for the kinetic parameters obtained with the Mettler TA 3000 analyzer software. In particular, it is noted in [60] that confidence intervals for kinetic parameters should not differ by more than 10% from the quantities themselves; the kinetic parameters calculated for different segments of kinetic curves should not be more than 10% different; the parameters should not depend on the heating rate, and the times of achieving one and the same transformation degree found from the reaction order under iso- and nonisothermal conditions should coincide.

In addition to the above statistical characteristics (correlation coefficient, residual sum of squares), various averages and average absolute deviations are used to fit the reaction order model [61–65]. All the approaches [61–65] are computer-aided, which greatly facilitates the kinetic analysis. This fact, however, does not increase the reliability, because of the restricted application of the model used in these methods.

When the IKP is solved by statistical methods, the kinetic parameters calculated by various methods often coincide [41, 42, 66–70]. Such a coincidence does not by any means point to the adequacy of the model found as a result of discrimination; it only corroborates the equivalence of the calculation procedures used. This can easily be inferred from [55]. It is shown in this work that the kinetic parameters calculated with the Freeman–Carroll and Horowitz–Metzger methods are in agreement, but their calculated values differ significantly from the true ones. Thus, the coincidence of the kinetic parameter values calculated via one and the same IKP solution method (discrimination) can not be a criterion of the proper choice of the model. Besides, the similarity of the numerical values of the kinetic parameters by no means points to their statistical identity. Thus, an example is considered in [71] when close parameter values cannot be regarded as consistent, while highly different parameters are statistically identical. Such a situation holds for highly elongated confidence regions characteristic of the IKP solution [72]. The identity of kinetic parameters estimated by different methods should be appropriately tested, for example, as in [73].

The above cited aspects of the IKP solution are far from all of the problems concerning the correct statistical processing of kinetic data. It seems necessary to list these problems and the ways to solve them.

First, in the great majority of cases, the kinetic parameters are calculated by linearizing the appropriate equation through a logarithmic transformation. Such a procedure markedly simplifies further calculations, though it is not quite correct, because of a random error that creeps into Eq. (1) (or a similar one) as an additive component. The logarithmic transformation distorts [13] Gaussian distribution, the parameters obtained being shifted. This effect is well known in statistics [74] as "regression displacement to the past". Thus, nonlinear calculation methods whose advantages are noted in [20, 75–83] should be preferred in interpreting the kinetic data. Among them, paper [83] requires special emphasis, as with this method it is possible to estimate both the kinetic parameters and the error distribution model. Certainly, nonlinear regression does not basically reduce the ambiguity [84]. However, the sensitivity of nonlinear Eq. (1) to the form of the formal model increases relative to the linear one [85].

Secondly, statistical processing of kinetic data, as a rule, is realized on the assumption that the random error is only included in the dependent variable. This assumption is simplified, however, due to the limited measurement accuracy of the dependent variable (time and especially temperature). Therefore, the regression methods used to process the kinetic data should take account of the errors in both variables [74]. The methods are detailed in [86–88].

Thirdly, it should be noted that statistical processing generally requires an assumption of the normal (Gaussian) distribution of errors. The validity of this assumption, which can be ascertained via appropriate tests [17], is not usually verified. As noted in [74, 89], the Gaussian model is too stringent for real data, and the excesses are more typical for them than follows from normal distribution. The kinetic parameters estimated with the least squares method are only optimum for normal distribution [74]. In this connection, the statistical apparatus gains special importance in obtaining robust estimates [74, 89, 90]. Such estimates, as noted earlier [8, 13], are required to process kinetic data. The excesses of experimental data can also be eliminated by smoothing with the aid of different filters [91–93]. It should be remembered, however, that any smoothing shifts the kinetic curves and, thus, the parameters of the smoothed curves will also be shifted. This fact presumably accounts for the essential increase of the kinetic parameters [93] calculated with the smoothed curves as compared with the reference ones, resulting from a shift of the curves to higher temperature region.

We believe that these are the three main problems that have lacked appropriate attention of late in the statistical processing of kinetic data. The solution of these problems will certainly provide more realistic results as compared with those obtained by conventional methods. Nevertheless, it should be remembered that, along with the shortcomings of statistical discrimination so far noted, there are some arguments against it on the whole. As shown in [21], the accuracy of experimental data is often insufficient to discriminate some models. The authors of [94] have drawn a more pessimistic conclusion: the IKP solution can be obtained within 10% accuracy provided the vector of the measured quantities is known as accurately as 0.0001%. One more limitation of statistical discrimination procedures and of the estimation of the kinetic parameters lies in the fact that none of these procedures is adopted as a standard [95]. Meanwhile, as noted above, the use of different statistical characteristics may result in different IKP solutions. However, the argument in [96] is most convincing to state that, in choosing the best model from the set of them, we ought to compare two statistical hypotheses. One of them assumes that experimental data can most appropriately be described by a single model. The other implies that the whole set of discriminating models gives their best description. As fairly noted in [96], the latter hypothesis is so general that it can describe any data within any accuracy and with higher accuracy, if anything, than the former hypothesis. As a result, the choice of the "best" model becomes meaningless, since the latter hypothesis is always better than the former from statistical grounds [96].

To conclude the section dealing with the application of statistical discrimination methods used to solve IKP's, we shall formulate its main points. In using statistical methods, it is not advisable for one to restrict oneself to a single model with an adjustable parameter (the reaction order or Avrami–Erofeev models). Once a single model has been chosen via the extreme statistical characteristics, it should be tested for homogeneity in order to reveal statistically equivalent models. When an unambiguous solution can be obtained, it should be taken into account that the solution is probabilistic, i.e. it is a single one within some confidence probability. Such a probability is relative, however, as it reflects the interpolation properties of the chosen model with reference to the ones used to discriminate the models rather than with reference to the real process [97].

Discrimination methods utilizing additional theoretical physico-chemical information

The methods in this group allow the IKP solutions to be discriminated by utilizing additional information derived within some theory concerning the processes under study or the properties of Eq. (1). In other words, within a certain theory, conventional information obtained in the kinetic experiment (kinetic curve) may be interpreted as additionally required to discriminate the IKP solutions. To be specific, theoretical estimates of the activated complex vibration frequency impose certain restrictions on the pre-exponential factor. Such restrictions allowed the authors of [96] to discount one of two competing models when they had failed to do so by statistical discrimination. However, the restrictions imposed on the pre-exponential value do not yield an unambiguous IKP solution. Thus, such restrictions, when used to discriminate formal models for calcium oxalate decomposition, have given rise to three equally justified models with the pre-exponential between 10^{11} and 10^{15} 1/s [99]. In this connection, it was suggested in [99] that the empirical relationship between the reaction order value and the degree of transformation at maximum rate be used as an additional criterion. Thus, by comparing the transformation degree, calculated in terms of the reaction order via the empirical formula [99], with its experimental value, we can choose the best model, as was done in the cited work. Wide use of such an additional criterion, however, is as problematic as the universal application of the reaction order model criticized in the previous section, since the formula in [99] holds for this model alone. As concerns the range restricting the pre-exponential value by the activated complex vibration frequency, namely 10^{12} to 10^{14} 1/s [98], 10^{11} to 10^{15} 1/s [99], it is seen to be too wide to be consistent with multiple IKP solutions. There is no need at all to discuss the applicability of these values to solid-phase processes.

By transforming basic Eq. (1) and assuming a definite form of the model, we can derive equations to relate the kinetic parameters and the coordinates of representative points on the kinetic curve. Additional information is obtained in this case as the basis for discrimination on the purely theoretical assumption that it is feasible to describe various solid-phase processes by the reaction order model or Avrami–Erofeev equation. For instance, the authors of [100, 101] suggested methods of calculating kinetic parameters from the temperature, the degree of transformation and its derivative at the maximum point of the kinetic curve. The process is assumed to obey the reaction order model, whose value is determined by the maximum point coordinates. Similar methods are argued in [102] and a method is considered [100] in its iterative version. It is found that the kinetic parameters determined via single point coordinates require that the maximum temperature measured be at least as accurate as 3 deg, and that the degree of transformation be no less than 0.025 and its derivative no less than $5 \cdot 10^{-5}$ 1/deg. It is stated in [102] that the methods in this group will fail to give a satisfactory description if all three values involve such errors.

Assuming that the process can be described by the reaction order or the Avrami–Erofeev models, relations were derived [103] for the kinetic parameters and temperatures at which the third derivative of the nonisothermal curve is zero. It is recommended that the form of the model be found from isothermal data. Other methods of determining kinetic parameters from three [104] or four [105] nonisothermal curve points are also known. These are based on the reaction order model and are iterative.

The common limitation of the methods [100–105] is that they are bounded within a single (reaction order or Avrami–Erofeev) model. Its universal use has already been commented on in the discussion of statistical discrimination methods. In fact, the discrimination by the methods [100–105] is a priori bounded within one model with a fitting parameter whose applicability is not corroborated. Further, as a very small number of points are used to estimate the kinetic parameters, the probability of errors is rather high. Accordingly, in general, the IKP solution via the representative kinetic curve points can only be recommended for a rough estimation of the kinetic parameters.

As analysis of Eq. (1) has shown [106] that the kinetic parameters calculated with the appropriately chosen model are independent of heating rate. This situation seems to stem from one fundamental postulate of formal kinetics, implying the independence of the kinetic parameters from the experimental conditions. It can be used as additional information to discriminate IKP solutions. The criterion of the independence of the kinetic parameters from the heating rate was used [106] to choose a model for the catalytic decomposition of potassium perchlorate. The kinetic parameters calculated in terms of this model are in much better agreement with isothermal values than are those calculated with other models [106].

In view of the criterion proposed in [106], it will be of interest to analyse the data obtained by different authors who applied statistical discrimination methods for the IKP solution. Thus, the dependence of the kinetic parameters on the heating rate was observed in [31, 36, 107–109]. In [107] alone, the dependence of the heating rate on the activation energy is not systematic, and therefore there is no reason to consider the choice of the model as incorrect. In other cases [31, 36, 108, 109], an essential decrease in the activation energy with increasing heating rate is observed. Following the criterion in [106], therefore, the models in those works were inappropriately chosen. The criterion of IKP solution discrimination offered in [106] is at the same time the technique used to test whether the models chosen by other discrimination methods are chosen correctly. It should be noted that such testing requires several nonisothermal runs. In this case, however, kinetic parameters can be calculated without choosing a specific model, i.e. by ignoring discrimination altogether. As will be shown below, just such an approach seems to be the most reliable.

The authors of [110] have advised that the IKP be solved with nonisothermal data, using isothermal experimental results that were supported in [111–113]. The method suggested the choice of a model of the process via isothermal experimental data, and then calculation of the kinetic parameters for nonisothermal data. Such a discrimination relies upon the theoretical statement that the formal process mechanism is independent of the experimental conditions. Within the statement, the information derived from isothermal kinetic experiments serves as additional information for discriminating IKP solutions. It should be remembered, however, that the model can be chosen via isothermal data provided the IKP solution, which is ambiguous in the general case, is known. The ambiguity of the IKP solution for isothermal data has already been illustrated [27, 32, 36]. The choice of the model by using isothermal kinetic data is undoubtedly more simple than in the nonisothermal case, as the number of competing models in the first case is always less than in the second. Nevertheless, a situation with no competing models is hardly possible. The ambiguous choice of the formal process model from isothermal data underlies the main limitation of the method. It implies that even a small error made in the choice of the process model with isothermal data may cause an essential error in the kinetic parameters calculated with nonisothermal data by using this model. This is due to the fact that, unlike isothermal data, for which the kinetic parameters slightly depend on the form of the model [48], kinetic parameters for nonisothermal data may vary by several orders, depending on the form of the model [114]. Therefore, the application of the approach suggested in [110] involves, in general, a certain degree of risk. For instance, such an approach was used in [115] to describe the magnesite and calcite decomposition kinetics. It was found in particular that, under isothermal conditions, both processes are described by the reaction equation for a process at an interface. The calculations of the nonisothermal kinetic parameters by using this model exhibited a slight increase in the activation energy for both magnesite and calcite decomposition: 131 to 139 kJ/mol and 155 to 176 kJ/mol with the heating rate rising from 2.5 to 15 deg/min. Thus, the IKP solution following [110] does not satisfy the above criterion for the correct choice of a model (from the heating rate-independence of the kinetic parameters). It should be noted here that the range of activation energies calculated in terms of nonisothermal data overlaps the isothermal value of 136 kJ/mol in the magnesite decomposition case alone. For the calcite instance, the isothermal value proved to be outside the corresponding range, and amounted to 179.5 kJ/mol.

We think it more reliable to use the approach which, to some extent, is in contrast with the one offered in [110], i.e. calculation of the kinetic parameters via isothermal data, with subsequent choice of the formal model from nonisothermal results. This model-must yield kinetic parameters mostly close to the isothermal ones. The discrimination method as such presumably relies on the aforesaid theoretical statement on the independence of the kinetic parameters from the experimental conditions. A similar approach was used in [116]. This takes account of the main advantage of isothermal data in the IKP solution: the kinetic parameters are weakly dependent on the model. Again, it makes use of the high sensitivity of the kinetic parameters towards the form of the model, which is typical of nonisothermal data. It should also be noted that a pure nonisothermal version of such an approach to the IKP solution is also possible. Thus, in [117] the results of the several nonisothermal experiments were used with the method of invariant kinetic parameters [118], which does not require the explicit form of the model for parameter calculation, to seek the activation energy and pre-exponential values. A formal model which describes experimental data in the best way was discriminated in accordance with the invariant kinetic parameters. A similar comparison of the kinetic parameters, calculated without choosing a process model in an explicit form and using the methods based on discrimination, was made in [119–122]. The agreement [119, 122] of the parameters obtained with different IKP solution techniques (with discrimination and without it) may be regarded as a criterion of the proper choice of the process model, in contrast with the agreement of the parameters calculated by different methods within one and the same IKP solution approach (discrimination) [41, 42, 66–70].

An original IKP solution method has been offered in [123]. It classifies the kinetic parameter calculation and formal model discrimination procedures in accordance with the results of several nonisothermal experiments. The kinetic parameters are computed via the temperature at which one and the same degree of transformation is achieved at different heating rates (isoconversional method). The models are discriminated over the transformation degrees and time for one and the same temperature at different heating rates (as in the case of isothermal conditions). The method was verified for the model data to prove its adequacy.

All the methods of discriminating formal models with respect to the consistency of the kinetic parameters derived in different IKP solution approaches are limited by the fact that the parameters change discretely depending on the form of the model. Therefore, there may be no agreement at all between kinetic parameter calculations that ignore explicit—form models and those based on discrimination of any kind. Complete discrimination will evidently be hindered in this case. For such discriminations, it is advisable to perform statistical homogeneity tests [73] for the parameters obtained by different methods.

We shall conclude this section dealing with theoretical discrimination methods by emphasizing their advantages. First, these methods ignore physically meaningless IKP solutions. Secondly, they provide consistent kinetic parameters calculated for different experimental conditions, such as iso- and nonisothermal conditions or at different heating rates. This is the main asset of the theory-based discrimination. However, such discriminations have a common limitation: none of them yields an ambiguous IKP solution. In the case of theoretical discrimination, this shortcoming directly indicates that various theoretical statements never provide an unambiguous discrimination criterion. Theory is only exact for general trends and laws whose particular forms are always specific for particular entities. It is therefore possible to specify a wide range of reasonable values of kinetic parameters rather than rigid boundaries for negligible deviations of the parameters derived under different experimental conditions.

Other discrimination methods

Two IKP solution methods will be discussed in this section. These include the discrimination experimental design [124] and Tikhonov's regularization [2]. Both are more rarely used than the above approaches. However, a brief discussion of them is desirable since Tikhonov's regularization is a general approach to the solution of inverse problems, while the discrimination experimental design is widely used in the kinetics of homogeneous reactions and is now being adopted in thermoanalytical practice [125].

The design of discriminating experiments consists in searching for experimental conditions under which the measurements are noninvariant when one competing model is substituted for another [124]. In this case, discrimination relies upon the information obtained as a result of a series of successive experiments, with each subsequent experiment designed by using the information derived from the previous one. The formal model chosen from such discrimination will possess the highest interpolation properties under a wide range of experimental conditions. However, it does not mean that this model completely represents the process under study and may be considered a true one [97]. Further, discrimination being possible only under certain experimental conditions [124], the IKP ambiguity is likely to hold true under other conditions.

Tikhonov's regularization method allows one to discriminate the IKP solution by using information on the solution properties [2] (smoothness, monotony, convexity, etc.). Additional conditions imposed make it possible to derive a single solution to the inverse problem, whose particular form will depend on the condition imposed. In this case, ambiguity manifests itself in the fact that a set of inverse problem solutions will be consistent with the set of conditions imposed. The regularization method as applied to the IKP solution is considered in [126]. It can also be used to solve inverse thermodynamic problems [127].

The regularization technique is basically close in essence to the discrimination methods based on theoretical considerations. Thus, it is noted in [2] that this method can be regarded as formalization and justification of the regularization method from common sense. It has been emphasized in [128] that the restrictions applied in the regularization method are artificial. It is also worth noting that Tikhonov's regularization is intimately connected with the statistical inverse problem solution and "ridge" regression [74], in particular. The coincidence of the "ridge" estimates with the regularized solution is considered in [129]. Possible experimental designs aimed at solving inverse problems by different methods, regularization included, are dwelt on in [130]. The monograph [131] is devoted to the software for Tikhonov's regularization and contains FORTRAN program texts.

Criticism of discrimination as an IKP solution method. Search for an alternative

The previous sections concern different versions of one IKP solution approach (discrimination) based on an unambiguous description It can readily be seen that none of the discriminations considered provided an unambiguous IKP solution. In other words, all the "unambiguous" discriminated solutions exhibited camouflaged ambiguity in a thorough analysis. Obviously, this limitation reflects imperfection of the discrimination methodology rather than that of the specific discrimination methods. In this section, we shall present arguments against the discrimination methodology whose analysis outlines the alternative IKP solution methodology.

Let us consider in brief the main features of the discrimination methodology. This methodology is based on the unambiguous description principle, consisting in a mandatory choice of the single "best" formal process model to estimate kinetic parameters. The unambiguous description principle implies, in fact, that there exists a true model of the process under consideration. Such an assumption causes no doubts. However, a problem arises here because the model is chosen from some arbitrary set, i.e. depending on a researcher's subjective considerations, and we are always unaware as to whether it includes the true model [97]. Any discrimination always offers some set of "best" models from the above set. The researcher is not sure, however, that the "best" models include the true one unless he possesses direct information about the process mechanism. Hence, the grounds for future ambiguity are laid down at the earliest IKP solution stage, i.e. when the set of models for discrimination is being chosen.

Naturally, the question arises of whether it is possible to derive an unambiguous IKP solution if the true model is included in the initial set of models to be discriminated. It seems to be possible only as an exception that proves the general rule which negates such possibility. We shall point to two reasons which do not allow an unambiguous discrimination even in such an artificial situation. The first reason implies that many of the classes of formal models cannot be distinguished in principle [132, 133] or at a certain error level [121]. This has the result that whole sets of models, including the true one, turn out to be the "best" discrimination models. The second one is due to the fundamental problem: for real solid-phase processes, how true can conventional elementary models [13, 14] be whose imperfection was noted in [134]? A practical reduced-coordinate analysis of the agreement between the kinetic curves obtained for isothermal conditions and the model ones often shows that real processes are intermediate, i.e. they are not consistent with any of the formal models [115, 135–139].

Evidently, in the general case the elementary formal models are too simple to allow for all features of real processes. Complication of the models results in a great number of various empirical parameters; if the numerical values of these are appropriately chosen, they can describe any curves. The attempts to achieve agreement between real processes and formal models in an experimental manner (by simplifying the process via the elimination of various external factors, heat and mass transfer, etc.) are restricted, on the one hand, by the practical requirements relating to the process conditions. On the other hand, even very sophisticated studies of monocrystal dehydration in vacuum prove that solid-phase processes are already macrokinetic at the micro level [140].

These, we think, are the main reasons why unambiguous discrimination is impossible in the general case. It should be remembered here that, even if a solid-phase model can be chosen unambiguously in same cases, the interpretation of the results will be ambiguous [141]. This stems from the fact that one and the same process model can be obtained from different assumptions on the mechanism underlying its derivation. For instance, in [142], the contracting sphere equation is derived from three different assumptions.

Accordingly, ambiguity of the IKP solution is bound to occur, due to the fact that real solid-phase processes are so involved that any formal models are always incomplete (imperfect) for them and, therefore, cannot be true. In turn, any incomplete model of the process provides an ambiguous description of it [143]. As it is generally impossible to reduce real processes to the formal model level, it follows that, in an analysis of ambiguity and a search for ways to overcome it, the main emphasis should be placed on how to improve the formal description of solid-phase processes.

The main paradox in the IKP solution is that formal models of the process are not truly the solutions to Eq. (1), i.e. they have been obtained independently of this equation and of particular experimental data. It is evident that the model solutions so obtained may describe a real process only to the extent to which some ideal process underlying this model reflects it [8]. Feasible derivation of more complete formal descriptions of the process is restricted because of the absence of the method of automatic synthesis of models [96], as the derivation of models is not amenable to algorithmic description [144]. It should be emphasized here that there is no method for the automatic synthesis of models in an explicit form. This means that, if a generalized description is available to represent any process in an implicit form (i.e. to describe formally the corresponding kinetic curve), the IKP solution can be obtained without any explicit form of the model set. Therefore, we hope that, as an alternative discrimination, the approach may be applied which uses some single generalized description by assuming a particular form depending on the experimental data, i.e. in the course of the IKP solution, rather than a "rigid" system of formal models. Such an approach will allow one to overcome the paradox encountered within the framework of discrimination methodology, because in this case the description of a process is synthesized from available experimental data and is therefore always in agreement with them.

The alternative approach to the IKP solution based on generalized descriptions exhibits the methodology which is basically different from discrimination. It relies on the complementarity principle, which offers a unique possibility to overcome ambiguity in all fields of knowledge [145]. This approach will be discussed in the second part of this review.

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Zusammenfassung — Diese Übersicht handelt von der Auswahl einer Methode zur Lösung des inversen kinetischen Problemes (IKP), welches die präziseste Beschreibung des Vorganges auch unter nichteindeutigen Bedingungen liefern kann. Zur Lösung des IKP Problemes sind zwei grundlegend verschiedene Methoden möglich: die erste beruht auf dem Prinzip der eindeutigen Beschreibung (Unterscheidbarkeit), während die zweite auf dem Komplementärprinzip (generalisierte Beschreibung) aufbaut. Die konkreten IKP Lösungsverfahren wurden auf der Grundlage ihrer methodischen Unterschiede klassifiziert. Im ersten Teil dieses Überblicks wurden allgemeine und spezielle Beschränkungen bei der Unterscheidung formaler Modelle untersucht.

Резюме — Обзор посвящен проблеме выбора метода решения обратной кинетической задачи, позволяющего в условиях неоднозначности получить наиболее определенные описания процесса. Отмечается, что возможны две принципиально различные методологии решения обратной задачи: методология, основанная на принципе однозначного описания (дискриминация), и методология, основанная на принципе дополнительности (обобщенные описания). С учетом различия методологических принципов проведена классификация конкретных методов решения обратной кинетической задачи. В первой части обзора проанализированы общие и специфические ограничения метода дискриминации.