Journal of Thermal Analysis, Vol. 36 (1990) 599-615

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

II. Methods based on generalized descriptions

S V. Vyazovkin and *A. I. Lesnikovich*

INSTITUTE OF PHYSICO-CHEMICAL PROBLEMS, BYELORUSSIAN STATE UNIVERSITY,
MINSK, USSR

(Received July 5, 1989)

The second part of this review deals with the methods of inverse kinetic problem (IKP) solving based on generalized descriptions of the process. The application of these methods is considered an alternative (for discrimination) approach to IKP solving. It is shown that the base of this approach is the methodology of complementarity. Different types of generalized descriptions, their merits and their shortcomings are discussed.

As noted in the first part of this review, the unambiguous description methods reduce the ambiguity of IKP solutions through discrimination by applying additional information. This information is regarded as external with respect to the data of a particular kinetic experiment, since it is only derived within certain assumptions of specific experimental conditions (on the distribution of random quantities, process nature, IKP solution properties, etc.). The applicability of these assumptions stems from general theoretical concepts rather than from the analysis of the kinetic curves described. In contrast with the discrimination methodology, the complementarity methodology implies the fullest possible use of internal information (i.e. that obtained in the particular experiment). Besides the difference in the origin of the information used, the complementarity methodology is characterized by the description of a process synthesized in the course of the IKP solution rather than presented by the a priori set "rigid" system of formal models. The methodological basis for generalized descriptions, their structure and their relationship with the IKP solution are considered in the following section.

IKP ambiguity from complementarity grounds

The "fatal" nature of the IKP solution ambiguity within the framework of discrimination methodology seems to have been understood most profoundly by Nalimov [1-3]. He noted that it is necessary to give up the search for a single best model and "to learn to comprehend the world phenomena, provided each of them is specified by a fan of models rather than by a single best model" [3]. The concept of "a fan of models", and also the idea [4] that a multitude of discriminating models possess a greater descriptive ability than any single model does, are the starting points in our understanding of the contribution made by the complementarity principle to generalized descriptions.

The complementarity nature of the formal models used to describe solid-phase processes is detailed in [5]. It should also be noted that complementarity arises from the very nature of formal models which are a formal mathematical description of idealized real processes. Therefore, any model is only able to describe certain properties of a real process common to those of an idealized process. In other words, every formal model describes noted has remained of model idealization corresponding to the real process. Real processes in the general case are intermediate with respect to ideal ones. Thus, it is clear that the formal picture of a process can be synthesized from the information on its individual features offered by a number of competing models. Such a synthesis is methodologically based on the complementarity principle, allowing all the variety of descriptions to be considered in terms of individual models as reflecting different but equally important features of a process.

The information advantages of the complementarity-based approach over those using discrimination are clear and strictly proved [6]. The comprehensive informativity of the complementarity methodology affords a more definite description of a process, exhibited in a more accurate description of the kinetic parameters for the IKP solution. The higher accuracy in this case follows directly from the inverse proportion between the error in estimating the parameters and the amount of information spent for its estimation [7].

The complementarity of formal models offers generalized descriptions of the model type. This is the situation with the Šestak-Berggren approach [8]. The generalized description in this method is the product of three power terms. Depending on the exponents, the generalized description may assume a form consistent with any of the conventional solid-phase reaction models used in kinetics [9, 10]. However, along with the models that apply a generalized description of the model type, there are an extensive group of methods which use a generalized description of the type of preexponential and formal model combination. They rely upon the general equation

$$\ln (\mathrm{d}\alpha / \mathrm{d}T)\,\beta = \ln [A f(\alpha)] - E / RT \qquad (1)$$

where $\mathrm{d}\alpha/\mathrm{d}T$ is the derivative of the nonisothermal kinetic curve; β is the heating rate; A and E are kinetic parameters; R is the gas constant; and T is temperature. It is obvious, once $f(\alpha)$ is independent of T, that the numerical values of parameter E and combination $A\ f(\alpha)$ can be determined unambiguously. A particular choice of the formal model is required, however, to estimate the preexponential factor. The latter varies with the form of the model, while the numerical value consisting with their combination is constant (in some way, it is the compensational effect of A and $f(\alpha)$). Such a relationship between the preexponential factor and the formal model is similar in form to a known uncertainty relation. This indicates, in particular, that the preexponential factor and the formal process model in Eq. (1) are complementary descriptions. The Piloyan [11] and the entire set of isoconversional [12] methods of kinetic parameter calculation illustrate the methods in this group.

Generalized model-type descriptions

As already noted, the methods of this group are represented by the Šestak-Berggren [8] approach using the generalized description of the form

$$f(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \qquad (2)$$

The Šesťak-Berggren equation, using the model in form (2), is often a redundant one, as the three power exponents cannot always be estimated from the experimental data, which results in turn in the first kind of ambiguity in the IKP solution. Thus, the analysis of Eq. (2) cited in [13] shows that no more than one parameter in (2) can be estimated. Our own studies, however, indicate that the number of parameters determined in (2) depends on the experimental data; two of the three parameters may be estimated within sufficient reliability. The reduced form of (2) (two power exponents) is also suggested in [9, 14]. Different procedures to calculate the parameters in (2) are offered in [15-17].

Equation (2) was applied in [18] in both its complete and reduced forms to describe the dehydration of $Ba(IO_3)_2.H_2O$. In all three possible applications of (2) in the form with two power exponents, the kinetic parameters turned out to be equal (E =67.8 kJ/mol, ln A =20) and very close to the values consistent with these for the complete equation (3) (E =68.2 kJ/mol, ln A = 19.4). In fact, this indicates that the kinetic parameters estimated with Eq. (2) in different forms are invariant under a particular form of the Šestak-Berggren model. The invariance of the kinetic parameters estimated within the Šestak-Berggren model is also supported by the coincidence of the kinetic parameters estimated using (2) and the Anderson isoconversional method [19] in [18] or the Kissinger method [20] in [21], which ignore the use of the implicit form of the process model for calculations. The independence of the kinetic parameters in the Šestak-Berggren method of form (2) seems to be a criterion for the reliability of the parameters obtained. The Šestak-Berggren approach, however, does not always display parameter invariance with respect to the form of the model (2) [22]. In this case, model (2) cannot be considered to be an ample generalized description and the values of the kinetic parameters cannot be taken as reliable. Nevertheless, a comprehensive comparison of the Šestak-Berggren approach with other methods based on model discrimination has demonstrated [16] its preferability.

Thus, the Šestak-Berggren approach can be applied to estimate reliable kinetic parameters. It should be remembered that, in this case, the reliability of the parameters is evidenced by their invariance to the form of Eq. (2).

The method suggested in [23] is among those using a generalized description of the model type. It is based on the classes of models rather than on individual formal models. Each class represents a two-dimensional subspace in multidimensional space of the functions that are mathematical equivalents of conventional models [9, 10]. The idea of two-dimensional space underlying the concept of a class of models [23] is ultimately bound up with the one to account for the ambiguity of the IKP solution given in [24]. It is pointed out there that all linearly-dependent models equally well describe one and the same process. It is obvious that the models covered by one class [23], two-dimensional space, are linearly related. Therefore, ambiguity encountered on choosing individual formal models and due to their linear relationship [24] disappears for the class of models which some process can be assigned to.

It is worth noting that the method based on model classes seems to be intermediate between two methodological approaches to the IKP solution. Thus, the method applies generalized descriptions (classes) characteristic of the complementarity methodology, but requires that the process be assigned to a certain class, i.e. to discrimination, as in the case with the methodology of unambiguous description. Owing to its duality, this method combines the advantages of a generalized description and the limitations of discrimination. Thus, if some process is assigned to a certain class, then this class is unambiguously chosen [23]. If the process is intermediate, which can be established by analysing corresponding relationships [23], its application is hindered. The method is therefore advisable to derive qualitative or semiqualitative information. The latter can be used, for instance, to solve the problem of the possible mechanistical description of a process by the Avrami-Erofeev or reaction order models, since the model varieties of this type are covered by different classes [23].

A linear combination of several formal models can be recommended as a generalized description [25]. Such a generalized description theoretically complies with some process consisting of several parallel reactions with close activation energies [26]. Linear combinations have shown [26] that Avrami-Erofeev type formal models can appropriately be substituted by linear combinations of formal models of three classes irreducible to one another [23] and describing power-law nucleation, interface reaction and diffusion. Hence, it follows in particular that, in addition to nucleation, the Avrami-Erofeev type models can describe some other complex processes. This means in fact that the Avrami-Erofeev model can in some instances possess the properties of a generalized description. As noted above, however, wide application of this model to describe various processes is problematic.

The probability spectrum of formal models seems to be more complicated in its structure than the above generalized descriptions [27]. Involving a discrete ordinal-number probability distribution of process description using individual formal models, these spectra are in fact a version of the idea proposed in [28]. It was noted there that solid-phase processes can hardly be described deterministically, and stochastic approaches are required for their description. The probability spectra [27] are mainly advantageous for their invariance under the experimental conditions if the latter do not change the process mechanism. Consequently, the probability spectra can be used to control the impact of the experimental conditions on the process behaviour. The limitations [27] primarily in the qualitative nature of all the information received.

The above generalized descriptions may include various approximating functions such as polynomials [9, 29, 30], splines [9], etc. It should be noted, however, that fitting the parameters of the corresponding function used instead of the formal model of the process is rather an intricate problem, whose solution in the general form [29] cannot be obtained without definite restrictions.

A remark concerning the reliability of the numerical values of the kinetic parameters obtained will conclude the section concerned with generalized descriptions of the model type. We have already noted that the methods of this group provide reliable kinetic parameters as geometric characteristics of the corresponding kinetic curve. However, the reliability of the parameters as the process characteristics is always a problem, as they are calculated from one kinetic curve. Thus in the case of a complex process (consisting of parallel stages with different activation energies), a change in the heating rate will change the geometry of the kinetic curve and, hence, the kinetic parameters. Accordingly, it can be concluded that the invariance of kinetic parameters obtained from generalized descriptions of the model type under the form of the model is their necessary criterion, their invariance under the heating rate being their sufficient criterion.

Generalized description of the model-preexponential factor combination type

Here, two versions of the application of combined model-preexponential descriptions will be considered. Both use Eq. (1), but the methods applied to obtain constant $f(\alpha)$ are different. One group includes the methods of calculating kinetic parameters from one kinetic curve. In this case, the assumption of $f(\alpha)$ = const is only approximately fulfilled for some α values. The other group is based on several kinetic curves. The assumption $f(\alpha)$ = const may strictly hold for a wide α range.

Methods based on one kinetic curve

Let us consider three methods [11, 31, 32] which are formally equivalent as they use one and the same kinetic equation (1). The difference between them consists in the experimental technique of obtaining the derivative kinetic curve (DTA [11], DTG [31]), or in the restrictions imposed on the interval of transformation degrees for the condition $f(\alpha)$ = const to hold.

Thus, it is shown that for the Piloyan method [11] the decomposition degree interval of 0.05 to 0.8 is admissible. The interval is almost the same (0.02 to 0.76) for the Fotiev procedure [31]. For the two methods, the activation energies calculated by iso- and nonisothermal data agreed in [11, 31].

The advantages of the Piloyan method were distinguished in studies on the kinetics of glass crystallization [33]. It is pointed out in [34] that this method, together with the corresponding analysis, will yield a satisfactory interpretation of the DTA measurements. It seems interesting to determine the power exponent in the Avrami-Erofeev equation as a ratio of the activation energy calculated by the Piloyan approach to the isothermal value [35]. Papers [36, 37] concern a pure nonisothermal determination of the Avrami-Erofeev index, i.e. by comparing Piloyan's activation energy and its isoconversional value. Such an approach, however, was criticized in [35, 38], via rejecton of the possibility of non isothermal determination of the Avrami-Erofeev index.

The Piloyan method has been analysed rigorously in [39]. The authors found that the errors in the activation energy calculated by this method exceed the values cited by 15 to 20 per cent [11]. Specifically, for experimental data consistent with the diffusional models, the relative error in the activation energy determination is above 50 per cent, while it is 142 per cent for the data obeying the Avrami-Erofeev equation (the power exponent being 1/3). Further, in the processing of the experimental data by the Piloyan method in [40, 41], it was noted that the appropriate relationships used in this method [11] are nonlinear. A comparison of the activation energies calculated by the Kissinger [20] and Šestak-Berggren [8] methods (both using generalized descriptions) and the activation energy calculated by the Piloyan method has revealed lower values for the latter method, while the values obtained by the first two methods are in agreement.

The criticism concerning the Piloyan method also seems to hold for the Fotiev method [31]. Both are limited by a problematic assumption concerning constant $f(\alpha)$ values in a wide α interval. This limitation may be overcome by taking account of the restrictions in [32]. It is suggested there that only a plane section of the kinetic curve characteristic of topochemical processes be used for calculations. The fair agreement of the activation energies calculated in [32] with the isothermal values supports the reliability of the method proposed.

It may therefore be concluded that, in application of the methods of this group, account should be taken of the interval of the transformation degrees for which kinetic parameters are to be calculated, as the reliability of the values obtained is mostly bound up with the legitimacy of the assumption $f(\alpha)$ = const. Owing to the great errors encountered in the Piloyan method, the latter and the Fotiev approach cannot be recommended for the calculation of values of the activation energies in a wide range of α. These methods, however, can be used to compare the activation energies, if it is sufficient to know the relative values. Additionally, all the criticism concerning the use of one kinetic curve to calculate kinetic parameters, dwelt on in the previous section, fully holds for these methods.

Methods based on several kinetic curves

Now consider the well-known methods proposed by Kissinger [20], Anderson [19], Friedman [42], Ozawa [43] and Flynn-Wall [44]. All these methods except the first one are isoconversional [12], i.e. constant values of $f(\alpha)$ in Eq. (1) (or its integral anamorphosis) are achieved by using temperature values for one and the same α value at different heating rates.

To determine the activation energy, the Kissinger method [20] uses the line slope on the coordinates $\ln(\beta / T_m)$–$1/T_m$ where T_m is the temperature corresponding to the maximum in the differential curves. Following this method, the finite equation is derived on the assumption that it is possible to describe the process by the reaction-order model. These are the two factors, the use of the temperature consistent with the maximum and the reaction-order model, that are criticized [45] in this method. Let us dwell upon these two factors.

Strictly speaking, the Kissinger method is not isoconversional, as the transformation degree α consistent with the temperature of the maximum differential kinetic curve depends on the heating rate [45]. The theoretical form of this relationship has been established in [46]. It is found there that the greater the activation energy and the value of β, the weaker is the dependence of α_m on β. Thus, at moderate heating rates and activation energies, the Kissinger method is practically isoconversional. It is pointed out in [47] that, for a process with an activation energy of about 100 kJ/mol and heating rates of from 5 to 20 deg/min, α ranges from 0.56 to 0.61 at random.

As concerns the limitations of the Kissinger method within the reaction-order model whose universal application was argued, its sphere of application is much wider than follows from the model underlying its derivation. As noted above, under certain conditions the Kissinger method is practically isoconversional. Here, the relationship to determine the activation energy ($\ln\beta / T_m - 1 / T_m$) asymptotically coincides with the relationship used in the isoconversional method [48], assuming that no model forms exist. Accordingly, the feasibilities of the Kissinger method are the wider, the greater the heating rates used and the activation energies for the process.

It is worth noting another aspect of the application of the method. In [49], the Kissinger method was improved by using the Avrami-Erofeev rather than the reaction-order model in it, which resulted, in the final analysis, in some transformation of the finite equation. As the Avrami-Erofeev model possesses rather a wide descriptive ability [50], the Kissinger method, when applied in version [49], will probably expand the field of its application as compared with the original version [20].

Papers [51-53] note that the Kissinger method provides activation energies close to the values obtained with isoconversional methods, which supports our opinion concerning its application. In all three cases [51-53], the activation energy exceeded 100 kJ/mol. Further, it is found in [54] that use of the temperature consistent with a definite transformation degree rather than the maximum temperature in the Kissinger method results in the coincidence of the activation energy estimates obtained by the Kissinger and Ozawa methods [43]. The modified version [49] of the Kissinger method is dwelt upon in [55, 56]. It is noted in [55] that the activation energy estimates obtained are practically the same as in the original Kissinger method. Fair agreement of the activation energies and isothermal values is pointed out in [56]. Such agreement for the Kissinger method is also found in [57]. Disagreement between the activation energy estimates found by the Kissinger method and the isothermal values is mentioned in [58] and exemplified in [45]. It is to be noted, however, that such disagreement is an indispensable but insufficient criterion for the imperfectness of the method, as the reasons for such an inconsistency may be physical or physico-chemical in nature.

Thus, it may be concluded that, including the above limitations, the Kissinger method can be applied to calculate the activation energies of a process. The sphere of its application, however, is somewhat narrower than in the case of the isoconversional methods considered below.

Consider now four classical isoconversional methods, displaying two different possible solutions of Eq. (1) either directly in a differential form (Anderson [19] and Friedman [42]) or in an integral form (Ozawa [43] and Flynn-Wall [44]). As already noted, these methods strive for a constant $f(\alpha)$ by using the data corresponding to the same transformation degree. It should be noted that the Anderson and Friedman techniques are equivalent, since the line slope on the coordinates $\ln\beta - 1/T_\alpha$ is used to calculate the activation energy, where α shows that the data stand for one and the same transformation degree. In the Ozawa and Flynn-Wall approaches, where the activation energy is determined by the line slope on the coordinates $\ln \beta$ - $1/T$, equivalence is displayed along the same lines. It should also be noted that the Ozawa and Flynn-Wall approaches are used more often than the Anderson and Friedman methods, as they do not require calculation of the derivatives.

Neither reviews nor monographs, unfortunately, give due attention to the isoconversional calculation methods. In [13, 59], the Kissinger method alone is mentioned; however, it can be considered isoconversional only under certain restrictions. In [60], a comprehensive criticism of the Ozawa method is given. Some criticism of this approach can be encountered in [9, 10], together with that of other isoconversional methods which state that several nonisothermal tests are required to calculate kinetic parameters. An unfavourable attitude to these methods has been displayed in their rare usage. Thus, none of the isoconversional methods is included among the seven most frequently applied methods [61].

Let us endeavour to give an objective consideration of the merits and demerits of these methods. Their undoubted merits seem to include the possibility of calculating, first, consistent kinetic parameters and, second, parameters consistent with isothermal values. Activation energies complying with the values obtained by other reseachers have been found in [58, 62-64]. Agreement with isothermal quantities is noted in [65-67], and [67] gives nineteen examples of such agreement. These merits make it possible to recommend isoconversional methods for the calculation of significant [68] activation energy values.

As concerns the demerits cited in the above works, they can hardly include the necessity for several nonisothermal tests [9, 10], because this is just the way to perform the reliable estimation of kinetic parameters. At the same time, it is truly noted in [60] that the dependence in the coordinates $\ln(\beta/T^2)$ - $1/T$ rather than that used in the Ozawa approach $\ln \beta$ - $1/T$ should be linear. This situation, however, is taken into account in the isoconversional method [48]. The following two disadvantages are more essential in the isoconversional methods. One disadvantage is that it is impossible to estimate the preexponential factor without knowing the form of the model. The other is due to the infrequently observed dependence of the activation energy on the transformation degree. Let us analyse these disadvantages.

Indeed it is impossible to determine the preexponential factor from the generalized description of the preexponential factor-formal model system type [60, 69], to say nothing that the feasibility of such a determination contradicts the complementary nature of the generalized description components. In this case, the preexponential factor values calculated for various models are different by several orders. The discrimination, so far criticized, yields an ambigous solution, and therefore seems to be unsuitable. The admissibility of different averagings in estimating the preexponential factor [43, 70] can hardly be justified, as the mean can only be estimated from among a series of uniform quantities. It is difficult to say to what degree preexponential factor values calculated for different models are uniform (of the same type). It is natural for isoconversional methods to estimate the preexponential from the compensational relationship [71] for the preexponential and activation energy. Application of the Arrhenius equation seems to be a sufficient condition for this relationship [72]. As isoconversional methods define the activation energy, then, following the compensation relationship, a certain activation energy value will evidently comply with a single preexponential. The compensation effect parameters can easily be obtained as regression line parameters. The set of Arrhenius doublets is estimated by using any procedure for kinetic parameters based on the explicit use of the model by variation of its form. We have applied this method in [73] and demonstrated its adequacy for model data. The method proposed for preexponential factor estimation can be applied when one kinetic curve is used for calculations [11, 31, 32]. This method does not contradict the complementarity nature of the formal model and preexponential factor, as it is determined independently in terms of the activation energy rather than in term of the complementarity description components (which is impossible on theoretical grounds). Thus, the first of the disadvantages of the isoconversional methods can easily be overcome. The case is more intricate as far as the second disadvantage is concerned, this being the sometimes encountered dependence of the activation energy on the transformation degree. It was observed, for instance, in [66, 74-77]. The demonstration of the activation energy as independent of the transformation degree can be found in [66, 78]. The nature of this dependence can be understood if it is recalled that it has been observed [79] during use of the isoconversional method to process model data complying with a system of two parallel competing reactions. It should be remembered that Eq. (1) underlying the isoconversional methods is the equation of a single-stage chemical reaction and its use to describe complex reactions is limited, as in this case the state of the system cannot be characterized by two quantities, T and α [80]. Complex processes that may be described by Eq. (1) include formally single-stage processes (those with a distinct limiting stage, parallel processes with close activation energy values, etc). Criteria for single-stage processes are suggested in [80], and may include the criteria for assessing the calculated activation energies put forward in [68]. It is noted in [81] that, if the kinetic curves are similar (affine), the activation energy is independent of the transformation degree. It should be remembered that the affine transformation of nonisothermal data, suggested, for instance, in [82], differs in its form from the corresponding transformation for isothermal data [83]. As a complex process violates the affinity of the curves plotted for the different heating rates, it can easily be shown [29] that the dependence of the activation energy on the transformation degree is a trivial consequence of the affinity violation. In view of this, the substitution [84, 85] of basic Eq. (1) by an alternative form, taking account of E *vs.* α in explicit form, cannot be admitted as sufficiently justified for two reasons. The first is that this relationship does not reflect the change in the activation energy with change in the process mechanism. It only represents a change in the mean activation energy of reactions that proceed at some instant corresponding to a definite transformation degree [86]. The second reason for the inadmissibility of substituting Eq. (1) is that this equation can fully account for the dependence of E and α [29].

An understanding of the reasons why the activation energy depends on the transformation degree suggests the ways by which this undesirable effect can be eliminated. It is natural in this case to use the model of parallel reactions, as was the case in [87, 88] to describe the dehydration of calcium oxalate monohydrate. Taking account of the inevitable difference in the specimens and the approaches used by the authors of [87, 88] to describe the dehydration of calcium oxalate monohydrate, it should be noted that the values of the kinetic parameters are very close and the models of the parallel processes are uniform. This kind of agreement of independent results is certainly a strong argument for the approaches suggested in [87, 88] and the approach in [89], developed to describe a complex process, which relied on the isoconversional principle [81, 89]. Therefore, the second limitation of isoconversional methods, when the dependence of the energy on the transformation degree is sometimes observed, should not in fact be ascribed to these methods, as it is due to the complex behaviour of the process and can be eliminated by describing the process within the complex reaction model.

Thus, if the advantages of isoconversional methods and of the ways of overcoming their disadvantages, are taken into account these methods are for the moment most efficient. Even if isoconversional methods do not provide reliable kinetic parameters, at any event they do reveal the complex nature of the process, which itself is information about its mechanism.

Isoconversional methods continue to develop. Thus, in [90] an approximation of the temperature range is proposed that is more accurate than Doyle's approximation [91]. It is pointed out in [90] that the calculation of kinetic parameters by using this approximation is simpler than the correction method suggested by Flynn [12]. Reich and Stivala have suggested a computer-aided version of the isoconversional method [92]. A particular version of the isoconversional method is considered in [93]. However, it requires a complicated heating programme to implement isokinetic conditions ($d\alpha/dt$ = const). Cycling heating [9, 68] makes it possible to employ the isoconversional method for tests with one and the same specimen. Ozawa's conception of generalized time [94], whose calculation requires that the activation energy be determined independently of the process model forms, is closely bound up with isoconversional methods. By using generalized time, it is possible in nonisothermal kinetics to go over to a single independent variable and to process kinetic data in a form similar to isothermal [95]. The introduction of generalized time will also extend the applications of Friedman's method [96].

The determination of invariant kinetic parameters in [97] is intimately bound up with the isoconversional method. Following the approach in [97], the kinetic parameters of a process are estimated as an intersection point of compensation lines obtained for different heating rates. Thus, in [98] it is found experimentally that invariant kinetic parameters coincide with the values obtained in [70] by using isoconversional methods. Moreover, this coincidence has been demonstrated theoretically (for model data) in [73]. A close connection between the method of invariant kinetic parameters and isoconversional methods also stems from the coincidence of the activation energies calculated by this and Kissinger's method. It is shown in [71] that the method of invariant kinetic parameters transforms the Arrhenius equation as

$$d\alpha / dT = \hat{A} / \beta \exp(-\hat{E} / R\hat{T}_i) \exp(-E_j / R\hat{T}_i) \exp(-E_j / RT) f_j(\alpha) \quad (3)$$

where ^ refers to invariant quantities; i and j are the ordinal numbers of the heating rate β and formal model $f(\alpha)$. The isoparametric (invariant) temperature $\hat{T}_i$ for the known heating rate β_1 is determined as the abscissa of the intersection point of the Arrhenius lines corresponding to formal models of the, $f(\alpha)$ set. It is evident that the value of $\hat{T}_i$ so determined is independent of the formal model $f_j(\alpha)$. On the other hand, it is shown in [99] that the temperature T_m complying with the differential kinetic curve maximum is not dependent on $f_j(\alpha)$ either. Therefore, it may be assumed that $\hat{T}_i = T_{m,i}$ [71]. With regard to the equality, the product of the two last exponents in (3) is unity, while Eq. (3) proper becomes

$$d\alpha / dT = \hat{A} / \beta_i \exp(-\hat{E} / RT_{m,i}) f_j(\alpha)$$

Hence, the Kissinger equation

$$d[\ln(\beta_i / T_{m,i}^2)] / d(1 / T_{m,i}) \approx -\hat{E} / RT \tag{4}$$

can easily be obtained (cf. transformation in [48]).

Identity (4), being proved, allows two conclusions. First, (4) indicates that the Kissinger equation can be obtained without any assuptions on the form of the formal model and is a particular case of the general equation (3) underlying the method of invariant kinetic parameters. Second, taking account of (4), it may be stated that the method of invariant kinetic parameters can be regarded as isoconversional in the same measure as can the Kissinger method.

An apparent compensation relationship, whose parameters are calculated with the use of a wide set of formal models $f_j(\alpha)$ by varying j, is a generalized description in the method of invariant kinetic parameters. The simultaneous use of several compensation relationships obtained for different heating rates, in the method of invariant kinetic parameters, permits the determination of both the activation energies and the preexponential factors, without assuming a particular form of the model. It is worth emphasizing that the application of the apparent compensation effect proposed earlier [73] allows an unambiguous estimation of the preexponential factor consistent with the activation energy calculated by the isoconversional method. The common calculation procedure in the isoconversional method and that of invariant kinetic parameters gives rise to a similar IKP solution technique. This is supported in particular by the equivalent values of the kinetic parameters estimated by these approaches [73]. The potentialities of the method of invariant kinetic parameters and their connection with isothermal quantities in particular are carefully analysed in [100].

Conclusions

In conclusion, we shall highlight the main points from our work and formulate some recommendations that we hope may be of practical use in the IKP solution.

The application of the methodology of unambiguous description (discrimination) provides, in the general case, an ambiguous IKP solution (see the first part of this review). In this connection, we think it impossible to use the methodology of unambiguous description in nonisothermal kinetics, because of the strong dependence of the kinetic parameters calculated with nonisothermal data on the form of the model. It is possible, however, to use it for the IKP solution from isothermal experimental data, as in this case the kinetic parameters slightly depend on the form of the model.

It is advisable to apply the complementarity methodology (generalized descriptions) necessary to obtain reliable kinetic parameters in order to solve various problems in practice. This methodology is universal, i.e. it can be used in both iso- and nonisothermal kinetics.

If the arguments against the methodology of unambiguous description and for the complementarity methodology have not convinced the reader, the authors advise that particular attention be paid to the necessity of the correct processing of experimental data. If we have managed to convince the reader in favour of the complementarity in the IKP solution, then it is worth emphasizing once again that the kinetic parameters calculated in terms of generalized descriptions by one kinetic curve can only act as its reliable geometric characteristics. Estimation of the kinetic parameters in terms of a generalized description, based on several kinetic curves, will provide evidence as to whether the reliable geometric characteristics are reliable physico-chemical characteristics of a process.

References

1 V. V. Nalimov, T. I. Golikova, Logical Bases of Experimental Design, Metallurgis, Moskva, 1981 (in Russian).
2 V. V. Nalimov, Yavod. Lab., 44 (1978) 325.
3 V. V. Nalimov, Zhurn. Vses. Khim. O-va 25 (1980) 3.
4 V. I. Dimitrov, Simple Kinetics, Nauka, Novosybirsk, 1982 (in Russian)
5 S. V. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 32 (1987) 901.
6 S. V. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 32 (1987) 1145.
7 Y. Bard, Nonlinear Parameter Estimation, Academic Press, N. Y., e. a., 1974.

8 J. Šestak and G. Berggren, Thermochim. Acta 3 (1971) 1.
9 J. Šestak, Themophysical Properties of Solids, Academia Prague, Prague, 1984.
10 M. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the Solid State, Elsevier, Amsterdam, e. a., 1980.
11 G. O. Piloyan, I. D. Ryabchikov and O. S. Novikova, Nature 212 (1966) 1229.
12 J. H. Flynn, J. Thermal Anal., 27 (1983) 95.
13 K. Heide, Dynamische Termische Analysenmethoden, VEB, Leipzig, 1979.
14 V. M. Gorbachev, J. Thermal Anal., 18 (1980) 193.
15 P. S. Nolan and H. E. Lemay, Thermochim. Acta, 6 (1973) 179.
16 D. T. Y. Chen and K-W. Lai, J. Thermal Anal., 20 (1981) 233.
17 V. Swaminathan, N. S. Madhavan and D. Radhamony, Thermochim. Acta, 43 (1981) 371.
18 J. Leyko, M. Maciejewski and R. Szunewich, J. Thermal Anal., 17 (1979) 263.
19 H. C. Anderson, J. Polym. Sci., Part C 6 (1963) 175.
20 H. E. Kissinger, J. Res. Nat. Bur. Stand., 57 (1956) 217.
21 J. Kwarciak, J. Thermal Anal., 30 (1985) 177.
22 G. Baldassare and V. Amicarelli, J. Thermal Anal., 30 (1985) 339.
23 S. V. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 32 (1987) 249.
24 J. M. Criado and A. Ortega, J. Thermal Anal., 29 (1984) 1225.
25 S. V. Vyazovkin and A. I. Lesnikovich, Thermochim. Acta, 122 (1987) 413.
26 A. I. Lesnikovich, S. V. Vyazovkin and I. S. Romanovsky, J. Thermal Anal., 34 (1988) 85
27 S. V. Vyazovkin, I. S. Romanovsky and A. I. Lesnikovich, J. Thermal Anal., 34 (1988) 239.
28 V. Jesenak, 8-th ICTA'85, Bratislava, Thermochim. Acta 92 (1985) 39.
29 S. V. Vyazovkin and A. I. Lesnikovich, Thermochim. Acta 128 (1988) 69.
30 R. Bar-Gadda, Thermochim. Acta 34 (1979) 161
31 A. A. Fotiev and V. V. Mochalov, Zh. Neorgan. Khim., 13 (1968) 3147.
32 L. K. Avramov, Thermochim. Acta., 54 (1982) 337.
33 M. Lasocka, J. Thermal Anal., 16 (1979) 197.
34 S. Zeman and E. Zemanova, J. Thermal Anal., 20 (1981) 331.
35 J. Colmenero, J. M. Barandiaran and J. M. Criado, Thermochim. Acta, 35 (1982) 367.
36 A. Marotta and A. Buri, J. Thermal Anal., 16 (1979) 449.
37 A. Marotta, A. Buri and S. Saiello, J. Thermal Anal., 23 (1982) 239.
38 J. M. Criado, J. Thermal Anal., 19 (1981) 221.
39 J. M. Criado and A. Ortega, J. Thermal Anal., 29 (1984) 1075.
40 J. Morales, L. Hernan, L. V. Flores and A. Ortega, J. Thermal Anal., 24 (1982) 23.
41 M. Lalia-Kantouri, G. A. Katsoulos and F. D. Vakoulis, J. Thermal Anal., 31 (1986) 447.
42 H. L. Friedman, J. Polym. Aci., Part C, 6 (1963) 183.
43 T. Ozawa, Bull. Chem. Soc. Japan, 38 (1965) 1881.
44 J. H. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 323.
45 T. B. Tang and M. M. Chaudhri, J. Thermal Anal., 18 (1980) 247.
46 C. Popescu and E. Segal, Thermochim. Acta, 63 (1983) 381.
47 J. C. M. Torfs, L. Deij, A. J. Dorrepaal and J. C. Heijens, Anal. Chem., 56 (1984) 2863.
48 A. Irabien, C. Santiago and A. Araiz, J. Thermal Anal., 29 (1984) 1131.
49 J. A. Augis and J. E. Bennet, J. Thermal Anal., 13 (1978) 283.
50 G. Blumental, Z. Chem., 22 (1982) 49.
51 J. P. Elder and V. B. Reddy, J. Thermal Anal., 31 (1986) 395.
52 G. M. Reddy, V. K. Mohan, B. K. M. Murali and A. K. Chatterjee, Thermochim. Acta, 43 (1981) 61
53 P. K. Gallagher and M. E. Gross, J. Thermal Anal., 31 (1986) 1231.
54 A. A. Van Dooren and B. M. Muller, Thermochim. Acta, 65 (1983) 257.
55 E. Louis and G. Garcia-Cordovilla, J. Thermal Anal., 29 (1984) 1139.
56 N. P. Bansal, R. H. Doremus, A. J. Bruce and C. T. Moynihan. J. Amer. Ceram. Soc., 66 (1983) 233.
57 C. Bouster, C. Comel, P. Vermande and J. Veron, J. Thermal Anal., 20 (1981) 115.
58 Y. P. Khanna and E. M. Pearce, J. Thermal Anal., 26 (1983) 107.
59 W. W. Wendlandt, Thermal Methods of Analysis, Wiley, N. Y., 1974.

60 V. A. Logvinenko, Thermal Analysis of Coordination Compounds and Clatrates, Nauka, Novosybirsk, 1982 (in Russian).
61 N. J. Carr and A. K. Galwey, Thermochim. Acta, 79 (1984) 323.
62 J. D. Cooney, M. Day and D. M. Wiles, J. Appl. Polym. Sci., 26 (1983) 2887.
63 A. Ballisteri, G. Montando and C. Puglisi, J. Thermal Anal., 29 (1984) 237.
64 N. Fatemi, R. Whitehead, D. Pirce and D. Dollimore, Thermochim. Acta, 104 (1986) 93.
65 A. Marotta, A. Buri and F. Branda, J. Thermal Anal., 21 (1981) 227.
66 N. D. Topor, L. I. Tolokonnikova and B. M. Kadenatsi, J. Thermal Anal., 22 (1981) 221.
67 T. Keměny and J. Šestak, Közp. Fiz. Kut. Intéz. Prepr., 1985, N115, 26pp.
68 M. Reading, F. Dollimore, J. Rouquerol and F. Rouquerol, J. Thermal Anal., 29 (1984) 775.
69 S. Basan and D. Guven, Thermochim. Acta, 106 (1986) 169.
70 J. D. Cooney, M. Day and D. M. Wiles, J. Appl. Polym. Sci., 29 (1984) 911.
71 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 30 (1985) 677.
72 J. Pysiak and B. Sabalski, J. Thermal Anal., 17 (1979) 287.
73 S. V. Vyazovkin and A. I. Lesnikovich, Thermochim. Acta, 128 (1988) 297.
74 L. Hernan, J. Morales, A. Ortega and J. L. Tirado, J. Thermal Anal., 29 (1984) 491.
75 J. P. Elder, J. Thermal Anal., 29 (1984) 1327.
76 H. S. O. Chan and J. R. Lusty, J. Thermal Anal., 30 (1985) 25.
77 J. P. Elder, Thermochim. Acta, 95 (1985) 41.
78 P. K. Gallagher, J. Thermal Anal., 25 (1982) 7.
79 T. Ozawa, J. Thermal Anal., 7 (1975) 601.
80 A. G. Merzhanov, V. V. Barzykin, A. S. Shteinberg and V. T. Gontkovskaya, Thermochim. Acta, 21 (1977) 301.
81 A. G. Merzhanov, V. G. Abramov and L. T. Abramova, Zh. Fiz. Khim., 41 (1967) 179.
82 J. Meindl, I. V. Arkhangelskii and N. A. Chernova, J. Thermal Anal., 20 (1981) 39.
83 V. A. Bir, Kinetika i kataliz, 28 (1987) 550.
84 E. Urbanovici and E. Segal, Thermochim. Acta, 94 (1985) 399.
85 E. Urbanovici and E. Segal, Thermochim. Acta, 98 (1986) 385.
86 D. R. Dowdy, J. Thermal Anal., 32 (1987) 137.
87 Y. Masuda, Y. Ito, R. Ito and K. Iwata, Thermochim. Acta, 99 (1986) 205.
88 A. Romero and E. Garcia, Thermochim. Acta, 104 (1986) 71.
89 N. I. Vaganova, V. I. Rozenband and V. V. Barzykin in: Mater.8 Vses. Simp. po Goreniyu i Vzryvu, Tashkent, 1986. Chernogolovka, 1986, P. 108.
90 M. R. Kenan, Thermochim. Acta, 98 (1986) 263.
91 C. D. Doyle, Nature, 207 (1965) 290.
92 L. Reich and S. S. Stivala, Thermochim. Acta, 61 (1983) 361.
93 D. Fatu and E. Segal, Thermochim. Acta, 61 (1983) 215.
94 T. Ozawa, J. Thermal Anal., 9 (1976) 369.
95 T. Ozawa, Thermochim. Acta, 100 (1986) 109.
96 T. Ozawa, J. Thermal Anal., 31 (1986) 547.
97 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 27 (1983) 89.
98 A. I. Lesnikovich, S. V. Levchik and G. F. Levchik, J. Appl. Polym. Sci., 31 (1986) 1943.
99 M. Iwao, S. Yasuko and M. Mikiko, Gakugaku Zasshi (J. Pharm. Soc. Jap.), 104 (1984) 280.
100 S. V. Vyazovkin, A. I. Lesnikovich and I. S. Romanovsky, J. Thermal Anal., 34 (1988) 609.

Zusammenfassung — Der zweite Teil dieses Rückblickes beschäftigt sich mit Lösungsverfahren für das inverse kinetische Problem (IKP) basierend auf verallgemeinerten Beschreibungen der Prozesse. Eine Anwendung dieser Verfahren wird als alternative Näherung der Lösung des IKP betrachtet. Es wird gezeigt, dass die Grundlage dieser Näherung in der Methodologie der Komplementärität besteht. Verschiedene Arten von verallgemeinerten Beschreibungen, ihre Vorzüge und Mängel werden besprochen.