A Unified Approach to Kinetic Processing of Nonisothermal Data

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ABSTRACT

Basic problems of kinetic processing of nonisothermal data ascertained from thermal analysis measurements can be solved by isoconversional methods. Analysis of the dependence of the activation energy on conversion often permits the identification of the kinetic scheme for the process. This dependence may also be used to solve applied kinetic problems related to predicting the behavior of a substance outside the range of experimental temperatures. Methods for using this dependence for evaluating both the preexponential factor and the reaction model, as well as for detecting isokinetic relationships, have been discussed. Because all of these operations have a common origin in computing the dependence of the activation energy on conversion, isoconversional methods may be considered as a basis of a unified approach to kinetic processing of nonisothermal data. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The kinetic studies of thermally induced reactions in solids are traditionally performed [1,2] by thermal analysis methods which measure a change in an extensive property (e.g., enthalpy in DSC, difference in temperature in DTA, and mass in TG). Such measurements do not allow a change of a measured property to be separated into contributions from single reactions. Hence, the kinetics of single reactions occurring during thermal transformation are beyond the reach of thermal analysis methods. This in no way means that the latent complexity of a process can be ignored in kinetic processing of such data. A method of kinetic analysis should allow for a possible change of rate-limiting step (and associated Arrhenius parameters) of the process [3]. Nevertheless, the kinetics of thermal transformations are usually described [4,5] by eq. (1) of a single-step reaction

$$d\alpha/dt = k(T) f(\alpha) \qquad (1)$$

(where $f(\alpha)$ is the reaction model, α is the extent of reaction, $k(T)$ is the Arrhenius rate constant, T is the temperature, and t is the time). For nonisothermal conditions, when the temperature varies with time with a constant heating rate, $\beta = dT/dt$, eq. (1) is represented as follows

$$d\alpha/dT = (A/\beta) \exp(-E/RT) f(\alpha) \qquad (2)$$

(where A is the preexponential factor, E is the activation energy, and R is the gas constant). Equation (2),

as well as numerous approximations of its integral form (3),

$$g(\alpha) = (A/\beta) \int_0^T \exp(-E/RT)\,dT \qquad (3)$$

(where $g(\alpha) = \int_0^\alpha f(\alpha)^{-1}\,d\alpha$ is the integral form of the reaction model) underlies most of the methods of kinetic processing. Those which are used most frequently [4,5] employ data obtained under one heating rate along. These methods yield a single kinetic triplet (A, E, and the reaction model) for the overall process of the thermal transformation. This type of analysis does not allow for a possible change in the rate limiting step.

These simpler methods may also give ambiguous values of Arrhenius parameters, even in a rather artificial case of a single-step process. The ambiguity lies in the very concept of these methods which consists in fitting alternative reaction models to data to evaluate the Arrhenius parameters. The latter are, therefore, inevitably tied up with a reaction model. The problem here is that usually quite different reaction models fit the data equally well (from the statistical point of view) whereas the numerical values of the corresponding Arrhenius parameters crucially differ [6–8]. The commonly accepted approach (hereafter referred to as "discriminating approach"), which is discriminating competing reaction models with the aim to choose the "best" one, only disguises the ambiguity, but in no way leads to single-valued Arrhenius parameters.

The ambiguity of the kinetic triplet implies not only that its physical meaning is obscure, but also that its practical use in solving applied kinetic problems is very doubtful. The term "practical use" as used above implies predicting the behavior of a substance outside the range of experimental temperatures. Knowing values of the kinetic triplet, one can predict a dependence of α on t at an arbitrary temperature, T_0

$$\alpha = G[tA \exp(-E/RT_0)] \qquad (4)$$

or a dependence of α on T at an arbitrary heating rate, β_0

$$\alpha = G\left[(A/\beta_0) \int_0^T \exp(-E/RT)\,dT \right] \qquad (5)$$

(where G is a function inverse to $g(\alpha)$). Equations (4) and (5) hold true on the assumption that the kinetic triplet remains the same when passing from the experimental temperatures to the temperatures of interest. In the case of predictions, the ambiguity of the kinetic triplet entails such imprecise solutions that they have no practical value [9].
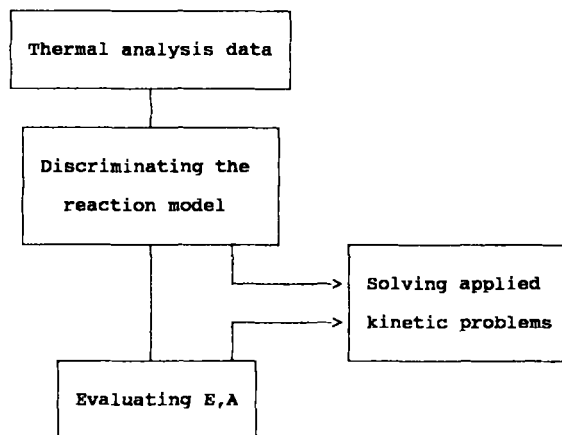

Figure 1 Scheme of the discriminating approach to kinetic processing of nonisothermal data.

Therefore, achieving trustworthy results under limitations of the familiar scheme (Fig. 1) presents a real challenge. The only way out of this situation is to abandon the traditional discriminating approach as a means of the kinetic processing of nonisothermal data. Isoconversional methods show considerable promise [10] as representatives of an alternative approach.

The intention of this article is to demonstrate that basic problems of kinetic processing of nonisothermal data can be solved by the use of the isoconversional methods. This in fact means that these methods may be considered as a basis for a unified approach to kinetic processing of nonisothermal data ascertained from thermal analysis measurements.

ISOCONVERSIONAL METHODS

Unlike the methods of the discriminating approach which number in several tens, the isoconversional methods are few. While these latter have been known for three decades, they have not gained wide exposure. One of the reasons seems to be the necessity of performing a series of measurements under different heating rates. However, such an approach allows evaluation of the activation energy unattached to the reaction model. Writing (2) in the logarithmic form for different heating rates β_i and considering it at a constant conversion

$$\ln[\beta_i(d\alpha/dT)_{\alpha,i}] = \ln[A_\alpha f(\alpha)] - E_\alpha/RT_{\alpha,i} \qquad (6)$$

(where the subscript α refers to the value related to a considered conversion, and i to a given heating rate). Equation (6) is at the basis of the isoconversional method proposed by Friedman [11]. If the mechanism

of the process does not depend on the heating rate, the $f(\alpha)$ value at $\alpha = \text{const}$ also does not depend on it. The slope of the plot $\ln[\beta_i(d\alpha/dT)_{\alpha,i}]$ against $T_{\alpha,i}^{-1}$ gives unambiguous (i.e., independent of the $f(\alpha)$-model) value of the activation energy related to a given conversion. The E_α value can further be evaluated by the integral isoconversional methods of Flynn–Wall [12] and Ozawa [13].

The isoconversional computations typically involve two difficulties. One of them arises when E_α varies substantially with α. Another resides in evaluating the two remaining components of the kinetic triplet. In this study a consideration is given as to how these difficulties can be treated to identify the kinetic scheme of the process and when solving applied kinetic problems.

IDENTIFYING THE KINETIC SCHEME OF THE PROCESS

A habitual notion "mechanism" is customarily used to designate a sequence of elementary steps involved in the process. Such a comprehensive information cannot be in principle obtained from thermal analysis data. Only those reactions which induce the change in the measured property are accessible to observation. In this respect, it would be reasonable to replace the term "mechanism" by a more confined one "kinetic scheme." The latter may be defined as a sequence of those steps which affect a change in a physical property being measured by a thermal analysis technique. the combination of thermal analysis with other techniques [1,2,14] is, however, capable of identifying the kinetic scheme closer to the mechanism.

It has been shown [12] that the isoconversional method applied to a multi-step process reveals the dependence of E_α on α. For this reason alone, this dependence should be considered as a source of kinetic information rather than as a difficulty to be overcome. Subsequently, it was shown [15] that this dependence helps, not only to disclose the complexity of a process, but also to identify its kinetic scheme as well. The shapes of the dependence of E_α on α have been identified from model data for competing [15], independent [16], consecutive [17], and reversible [18] reactions, as well as reactions complicated by diffusion [19]. The most characteristic dependencies are presented in Figure 2. Although the shape of the dependence of E_α on α does not necessarily unequivocally identify the kinetic scheme of a process, it in all instances sheds light on the latter.

An increasing dependence of E_α on α (1 in Fig. 2) is found for competing reactions [15], although some
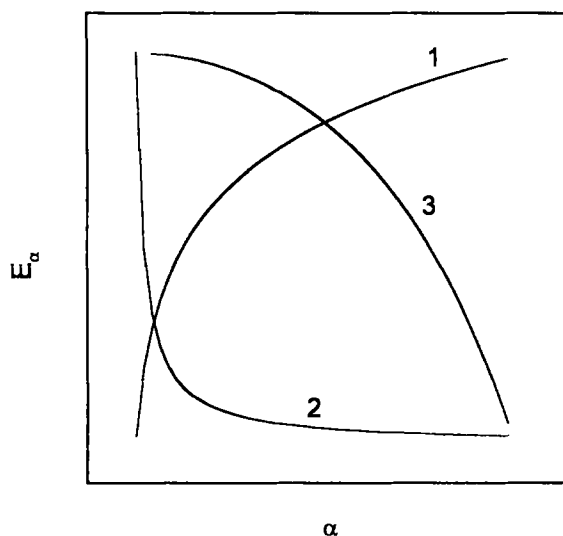
Figure 2 Dependencies of E_α on α characteristic of complex processes involving competitive reactions (1), reversible (2) reactions, and reactions complicated by diffusion (3).
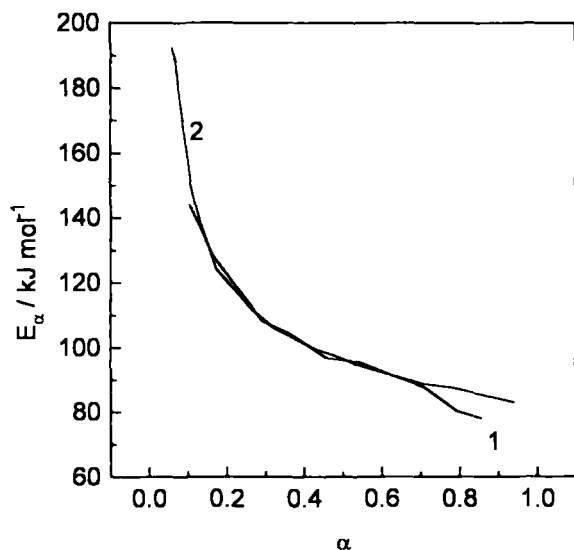
independent [16] and consecutive [17] reactions may also give rise to such a dependence. These dependencies (Fig. 3) have been observed for the thermal decomposition of polypropylene studied by thermogravimetry [20] and mass-spectrometry [21]. The shapes observed have been explained [20] by competition between pyrolysis and oxidation taking place in the presence of oxygen. Similar dependencies occurring in the absence of oxygen have been interpreted [21] in the context of the
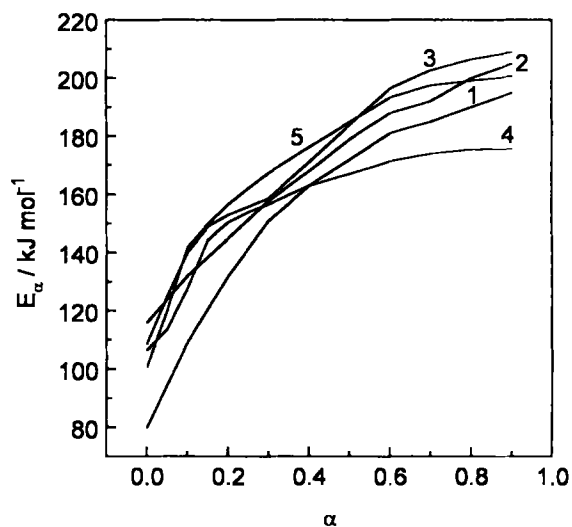
Figure 3 Dependencies of E_α on α for thermal decomposition of polypropylene studied by thermogravimetry [20] (in air (1) and in helium (2)) and mass-spectrometry [21] (constituents with $m/z = 41$ (3), 42 (4), and 43 (5)).

general mechanism for the thermal decompositions of linear polymers [22]. The depolymerization rate is affected by competition among decompositions of individual macromolecules and intermolecular associates. These interpretations are likely to apply to the thermal decompositions of many polymers. Increasing dependencies of E_α on α (or on T) have been discovered for the thermal decompositions of polystyrene [22] and poly(imide siloxane) [23] throughout the entire interval of conversions. Additionally such dependencies are often encountered at the beginning of the thermal decompositions of polymers. Examples here are poly(ethylene terephthalate) [24] ($\alpha < 0.7$), polyethelene [25] ($\alpha < 0.5$), and poly(butadieneacrylonitrile-acrylic acid) [26] ($\alpha < 0.25$).

It has been shown [18] that the decreasing dependence of E_α on α (2 in Fig. 2) corresponds to the kinetic scheme of an endothermic reversible reaction followed by an irreversible one. E_α is limited by the sum of the activation energy of the irreversible reaction and the enthalpy of the reversible reaction, at low conversions, and by the activation energy of the irreversible reaction at high conversions. The reversible dehydrations of crystal hydrates, as well as other processes involving a reversible step, demonstrate [18] these characteristic dependencies of E_α on α. A striking example is the dehydration of calcium oxalate monohydrate. This process is usually considered to be a reference single-step reaction when appraising new methods of kinetic processing of thermal analysis data. Figure 4 displays the dependencies [27,28] of

E_α on α for the dehydration of $CaC_2O_4 \cdot H_2O$. This process is thus a multi-step reaction which may be interpreted [18] as a change from the reversible dehydration to irreversible one when the temperature is increased.

The dependencies of E_α on α characteristic of the kinetic scheme of consecutive reactions have been examined in Ref. [17]. This scheme is applicable not only to the processes for which the existence of consecutive reactions is proven [29–31], but also to processes proceeding with a change from a kinetic to a diffusion regime. Such processes are widely met in solids decomposed in the following way: solid → solid + gas. As a surface layer of the solid product grows, diffusion of a gas through it gradually becomes the rate limiting step of the decomposition. Considering the original substance covered by a layer of the product as an intermediate, allows the kinetic scheme of consecutive reactions to be applied [19] to the above process. The latter features the characteristic dependence of E_α on α (3 in Fig. 2). Similar dependencies have been observed [19] for the thermal decomposition of wood (Fig. 5).

The influence of diffusion on this process is well known [32]. Furthermore, analogous dependencies have been established for the first step of decomposition of (NH_4) $[VO(O_2)_2(NH_3)]$ [33] and for curing epoxy resins [34]. In the latter example an important role of diffusion has been pointed out [34].

SOLVING APPLIED KINETIC PROBLEMS

Isoconversional methods identify the dependence of E_α on α for a reaction but do not yield the preexpo-

Figure 4   Dependencies of E_α on α for the dehydration of $CaC_2O_4 \cdot H_2O$ (the curves were plotted using the results from refs. [27] (1) and [28] (2)).

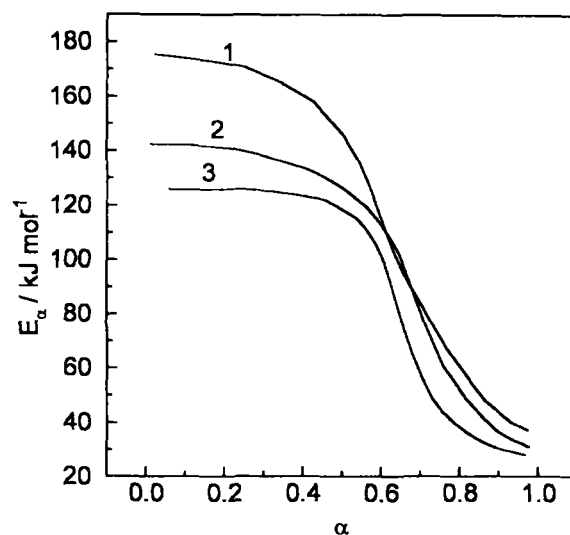Figure 5   Dependencies of E_α on α for the thermal decomposition of wood: pine (1), birch (2), and oak (3).

nential factor and the reaction model. A variation of E_α with α is often overcome by averaging [35–38] E_α over α. Since averaging should only be applied to randomly varying values, averaging of systematic dependencies [35–38] of E_α on α is statistically meaningless. This procedure might be justified when a change in E_α is several percent of the mean value [35], but not when such a change is comparable [37,38] to the mean value.

However the difficulties of extrapolation to other temperatures or heating rates can be overcome without averaging E_α and even without evaluating both absent components of the kinetic triplet. To do this requires modification of the assumption about retention of the kinetic triplet under changes of temperature. Such an assumption is not valid for the general case because an arbitrary process cannot be described by a single kinetic triplet throughout the entire interval of conversion. It is more reasonable to assume that the partial (i.e., related to a given conversion) kinetic triplets remain the same when changing temperature. Under this assumption we can equate the expressions (7) and (8) related to a given conversion

$$g(\alpha) = t_\alpha A_\alpha \exp(-E_\alpha/RT_0) \qquad (7)$$

$$g(\alpha) = (A_\alpha/\beta) \int_0^{T_\alpha} \exp(-E_\alpha/RT)\,dT \qquad (8)$$

which hold true under isothermal (T_0 = const) and nonisothermal (β = const) conditions, respectively. Simultaneous solution of (7) and (8) for t_α yields (9)

$$t_\alpha = [\beta \exp(-E_\alpha/RT_0)]^{-1} \int_0^{T_\alpha} \exp(-E_\alpha/RT)\,dT$$

$$(9)$$

(where T_α is an experimental value of the temperature corresponding to a given conversion at the heating rate β). Equation (9) enables the time at which a given conversion will be reached at an arbitrary temperature, T_0, to be computed.

Similarly, eq. (8) corresponding to different heating rates can be equated at the same conversion. Transformations lead to (10)

$$(1/\beta) \int_0^{T_\alpha} \exp(-E_\alpha/RT)\,dT$$

$$- (1/\beta_0) \int_0^{T_{\alpha,0}} \exp(-E_\alpha/RT)\,dT = 0 \qquad (10)$$

(where β and T_α are experimental values). $T_{\alpha,0}$ found as a solution of (10) is the temperature at which a given conversion will be reached at an arbitrary heating rate, β_0.

Solving (9) and (10) for different conversions, one can predict a dependence of α on t at an arbitrary

temperature, or/and a dependence of α on T at an arbitrary heating rate. Note that these equations do not incorporate both the kinetic model and the preexponential factor. So, provided that the assumptions made above are valid, these two components of the kinetic triplet are not necessary in extrapolating experimental results to other sets of conditions.

The absence of both the kinetic model and the preexponential factor in (9) and (10) means that these components do not introduce errors of their evaluation into a solution of applied kinetic problems. Additionally, the use of the complete dependence of E_α on α, in (9) and (10) takes into account the complexity of the process. A theoretical analysis of the errors arising in the dependencies of α on t predicted in various ways (including those given by (4) and (9)) has shown [39] that (9) as compared to different variations of (4) provides reliable results. Examples of inaccurate predictions made by (4) can be found in refs. [40 and 41].

Equations (9) and (10) have been successfully incorporated by Mellter–Toledo into kinetic software of TA 8000. With this software, the kinetics of curing epoxy resin (CY229, Ciba-Geigy) have been predicted. Figure 6 shows the results of predictions as compared to actual isothermal measurements.

Equations (9) and (10) have been used [42] to predict the influence of additives on the process of combustion of HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctan). The direct measurements of the combustion rates have confirmed [42] the predictions.
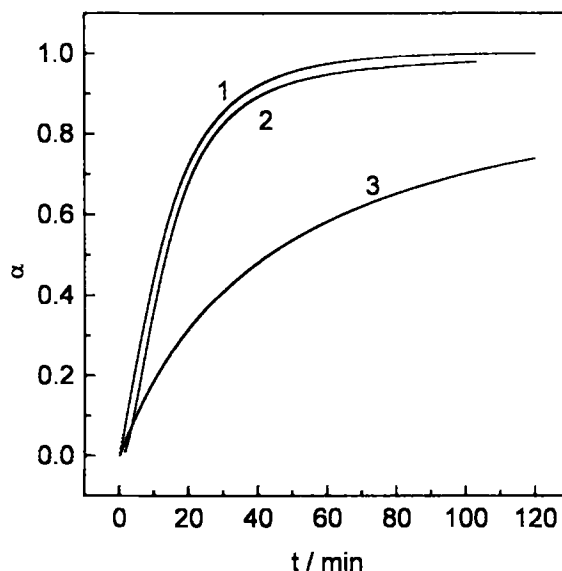
Figure 6 Conversion on time plots for curing epoxy resin at 130°C (measured (1) and predicted by eq. (9) (2) and eq. (4) (3)).

EVALUATING THE PREEXPONENTIAL FACTOR AND DETECTING ISOKINETIC RELATIONSHIPS

The foregoing shows that the preexponential factor and the reaction model are not required in identifying the kinetic scheme of the process and solving applied kinetic problems. However these components of the kinetic triplet can be evaluated [43]. A field of application of this method [43] is limited by the processes which obey a reaction model $f(\alpha) = (1 - \alpha)^n$. In a more general case, an actual value of $\ln A_\alpha$ can be estimated [44] by an artificial isokinetic relationship (IKR) (11)

$$\ln A_j = c + dE_j \qquad (11)$$

This IKR is inherent to the values of $\ln A_j$ and E_j computed by any method of the discriminating approach when varying the reaction models (e.g., when inserting diverse $f(\alpha)$ [4,5] in (2)). Once c and d have been evaluated, the E_α values are substituted for E_j in (11) to estimate the corresponding $\ln A_\alpha$ values. Clearly the resulting $\ln A_\alpha$ values will linearly depend on E_α. Such dependencies have been really observed [45,46].

A knowledge of both Arrhenius parameters provides a possibility of detecting isokinetic relationships [47,48] (IKR). A real IKR manifests itself both as a common point of intersection of Arrhenius lines and as an interrelationship (12) of Arrhenius parameters related to particular reactions of a single series

$$\ln A_n = a + bE_n \qquad (12)$$

(where subscript n refers to a particular reaction). The occurrence of an IKR has been explained [48] by a resonant vibrational energy exchange between reactants and their molecular environment. From this it is inferred [48] that the resonance frequency, ν_{iso}, is related to the isokinetic temperature, T_{iso}, as follows (13)

$$\nu_{iso} = k_B \cdot T_{iso}/h , \qquad (13)$$

(where k_B and h are Boltzmann's and Planck's constants accordingly). T_{iso} is evaluated by (14) through the b-parameter in (12)

$$T_{iso} = (Rb)^{-1}. \qquad (14)$$

If ν_{iso}, estimated by the experimental value of T_{iso}, is actually present [48,49] in the far IR-spectra, it is possible to specify a reaction group, the transformation of which is assumed to be the rate limiting step of the process.

Successive substitution of values of $\ln A_\alpha$ and E_α for reactions of one series into (12) and of b into (14)

gives the T_{iso} value for a given conversion. Analysis of the dependence of T_{iso}, as well as of a confidence interval for T_{iso}, on α can be used to detect real IKR's for multi-step reactions [50]. This method has been extensively tested [50,51] and applied to the series of thermal decompositions in poly(ethylene terephthalate) composites [50] and in tetranuclear copper(II) complexes [51]. In both series, vibrational frequencies evaluated by (13) agree well with the IR absorption bands assigned to specific groups. The assumptions about the reaction pathways have been confirmed [50,51] by independent experimental data reported in literature.

RECONSTRUCTING THE REACTION MODEL

Knowing the values of A_α and E_α, it is easy to reconstruct the reaction model in tabular form. Equation (8) allows the function $g(\alpha)$ to be reconstructed. To reconstruct $f(\alpha)$ eq. (15) can be used

$$f(\alpha) = \beta(d\alpha/dT)_\alpha [A_\alpha \exp(-E_\alpha/RT_\alpha)]^{-1}. \qquad (15)$$

An explicit form of the reaction model is identified by fitting the corresponding theoretical equations [4,5] to the tabular dependence of $f(\alpha)$ (or $g(\alpha)$) on α. It is apparent that such reconstruction of the reaction model is meaningful only for a single-step process an indication of which is independence of E_α on α.

CONCLUSION

The discussed sequence in kinetic processing of nonisothermal data is illustrated in Figure 7. All operations have their origin in the isoconversional computation of the dependence of E_α on α. This scheme,
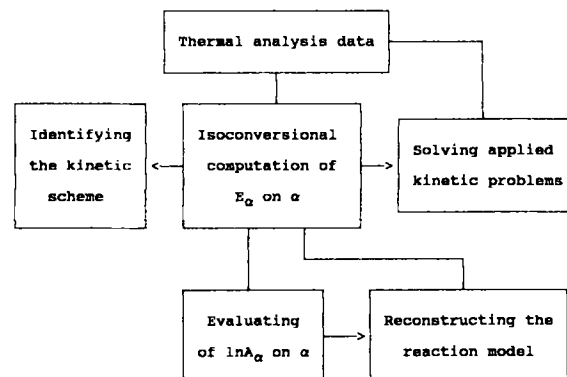

Figure 7   Scheme of a unified approach to kinetic processing of nonisothermal data.

because of two reasons, namely, that it covers basic kinetic problems and that it solves them on a single base, may be considered as a unified approach to kinetic processing of nonisothermal data ascertained from thermal analysis measurements.

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