

Isothermal and non-isothermal kinetics of thermally stimulated reactions of solids

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This review covers both the history and present state of the kinetics of thermally stimulated reactions in solids. The traditional methodology of kinetic analysis, which is based on fitting data to reaction models, dates back to the very first isothermal studies. The model fitting approach suffers from an inability to determine the reaction model uniquely, and this does not allow reliable mechanistic conclusions to be drawn even from isothermal data. In non-isothermal kinetics, the use of the traditional methodology results in highly uncertain values of Arrhenius parameters that cannot be compared meaningfully with isothermal values. An alternative model-free methodology is based on the isoconversional method. The use of this model-free approach in both isothermal and non-isothermal kinetics helps to avoid the problems that originate from the ambiguous evaluation of the reaction model. The model-free methodology allows the dependence of the activation energy on the extent of conversion to be determined. This, in turn, permits reliable reaction rate predictions to be made and mechanistic conclusions to be drawn.

1. Introduction

Interest in the reaction kinetics of solids was awakened in the early 20th century [1, 2]. At that time, the basic experimental techniques known today as differential thermal analysis (DTA), thermogravimetry (TG), and evolved gas analysis (EGA) were developed [1, 3–5]. The earliest kinetic studies were performed under isothermal conditions [1]. While non-isothermal methods were used [5] to follow the reaction rates in solids, the results of these studies were not used for kinetic evaluations until the 1930s [6]. Therefore, the concepts of solid state kinetics were established [7–11] on the basis of experiments carried out under isothermal conditions. Initiatory non-isothermal kinetic studies had been largely ignored, but Flynn [12] gave an enlightening review of pioneering work in non-isothermal kinetics.

Early kinetic studies [1, 2, 13–20] employed the currently accepted kinetic equation

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

where t represents time, α is the extent of reaction, T is the temperature, $k(T)$ is the temperature-dependent rate constant and $f(\alpha)$ is a function that represents the reaction model [21, 22]. Some of the reaction models are shown in table 1. The reaction models used in early kinetic works [1, 2, 13–20] were inherited from homogeneous kinetics. Obviously, these models could not account for the specific features of solid state reactions. For instance, Centnerszwer and Bruzs successfully described the thermal decomposition of Ag_2CO_3 [16] and MgCO_3 [17] as single-step first-order kinetics. Nevertheless, the kinetics of the thermal decomposition of CdCO_3 [18] and CoCO_3 [23] required the use of a more sophisticated model of two consecutive first-order

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Table 1. Set of alternate reaction models applied to describe thermal transformations in solids.

Reaction model		$f(\alpha)$	$g(\alpha)$
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	$1/2\alpha^{-1}$	α^2
6	Mampel (first order)	$1 - \alpha$	$-\ln(1 - \alpha)$
7	Avrami-Erofeev	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
8	Avrami-Erofeev	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
9	Avrami-Erofeev	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
11	Contracting sphere	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
12	Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$

reactions. The first attempts to develop authentic models of solid state kinetics date back to the late 1920s [24–28]. Further accumulation of experimental information gave rise to the development of more comprehensive kinetic models [29–35].

Interest in the temperature dependence of the rate of solid state reactions also arose during this period [23, 36, 37]. Bruzs [23] used the first-order reaction model and the Arrhenius equation [38]

$$k(T) = A \exp(-E/RT) \quad (2)$$

(A is the pre-exponential factor, E is the activation energy and R is the gas constant) to evaluate the activation energy of the thermal decomposition of several carbonates including ZnCO_3 . Later, Hüttig *et al.* [39] used a power law model ($n = 2/3$) to describe the thermal decomposition of ZnCO_3 and found a significantly smaller value of E ($38.4 \text{ kcal mol}^{-1}$) as compared to 95 kcal mol^{-1} found by Bruzs. This contradiction seems to be one of the earliest examples of the kinetic ambiguity, resulting in the fact that the same process can be described by various reaction models as well as by different activation energy values. Kujirai and Akahira [37] studied the effect of temperature on the decomposition rate of insulating materials. In their work, they used the empirical equation:

$$\log t = Q/T - F(w), \quad (3)$$

where w is the percentage weight decrease of the initial value, t is the time to reach the extent of decomposition w at different temperatures, and Q is a 'material constant' [37] that was determined as the slope of the plot $\log t$ versus T^{-1} line. The true meaning of Q and $F(w)$ in equation (3) can be illustrated by integrating equation (1):

$$g(\alpha) \equiv \int_0^\alpha [f(\alpha)]^{-1} d\alpha = k(T) t. \quad (4)$$

After substitution for $k(T)$ and rearranging, this yields

$$\ln t = E/RT - \ln [g(\alpha)/A]. \quad (5)$$

Then, Q in equation (3) is $E/2.303R$, and $F(w)$ is $\log [g(\alpha)/A]$. For a constant value of α , the second term in equation (5) is constant and E can be determined from the slope of $\log t$ versus T^{-1} regardless of the form of the reaction model. Therefore, Kujirai and Akahira [37] were in fact the first to propose the so-called isoconversional method of kinetic evaluations.

The problem of interpretation of experimentally determined Arrhenius parameters is often associated with the problem of applicability of the Arrhenius equation in solid state kinetics. The use of this equation has been criticized from a physical point of view [40, 41]. Garn [41] has stressed that the Arrhenius equation is meaningfully applicable only to reactions that take place in a homogeneous environment. However, this point of view seems to have ignored the fact that thermal decomposition has been successfully described [42, 43] in the framework of an activated complex theory that gave rise to Arrhenius-like expressions for the temperature dependence of the process. The Arrhenius equation has also allowed for descriptions of the temperature dependence of many thermally activated solid state processes such as nucleation and nuclei growth [44] or diffusion [45] presumably because the system must overcome a potential energy barrier, and the energy distribution along the relevant coordinate is governed by Boltzmann statistics. Even for cases in which the density of available states is sparse, Galwey and Brown have shown [46] that Fermi–Dirac statistics (for electrons) and Bose–Einstein statistics (for phonons) also give rise to Arrhenius-like expressions. Therefore, the use of the Arrhenius equation is not only justifiable in terms of a rational parameterization, but also its use and physical interpretation are supported by a sound theoretical foundation.

Nevertheless, a practical problem in the interpretation of experimentally determined values of E and A does exist, and it lies in the very nature of the experiments. Standard experimental techniques (e.g., TG, differential scanning calorimetry (DSC), DTA) as well as more sophisticated methods [10, 11] generally do not allow the isolation of elementary reactions. Rather, they provide a global measure of the rate or extent of a process that usually involves several steps with different activation energies. For this reason, experimentally derived Arrhenius parameters of a solid state process must be interpreted as effective values unless mechanistic conclusions can be justified by ancillary data.

Recently Flynn [47] gave an overview of alternative expressions to describe the temperature dependence of the reaction rate, none of which has been extensively used. However, we have to mention a work by Dollimore *et al.* [48] who used the Harcourt and Esson equation [49] to describe thermal decomposition kinetics in solids.

The first kinetic evaluations of non-isothermal data involved samples that were heated at a constant rate, $\beta = dT/dt$ [6]. To determine kinetic constants, Vallet [6] suggested replacement of the temporal differential in equation (1) by

$$dt = dT/\beta. \quad (6)$$

This rather trivial transformation bears a great physical meaning. It implicitly assumes that the change in experimental conditions from isothermal to non-isothermal does not affect the reaction kinetics. Intuitively, this assumption feels quite reasonable, at least as long as we are dealing with a simple single-step process. However, for multi-step reaction kinetics, it may have serious implications that are discussed later.

The explosive development of non-isothermal kinetics began in the late 1950s when thermal analysis instruments became commercially available. Since that time there has been an ever increasing number of works dealing with methods of determining Arrhenius parameters and the reaction model from non-isothermal experiments [50–63]. The initial enthusiasm was spurred on by the practical advantages of the non-isothermal experiments. Firstly, non-isothermal heating resolved a major problem of the isothermal experiment, which is that a sample requires some time to reach the experimental temperature. During the non-isothermal period of an isothermal

experiment, the sample undergoes some transformations that are likely to affect the results of the following kinetic analysis. This problem especially restricts the use of high temperatures in isothermal experiments. Secondly, because a single non-isothermal experiment contains information on the temperature dependence of the reaction rate, it was widely believed [52–58, 62, 63] that such an experiment would be sufficient to derive Arrhenius parameters and the reaction model of a process. Up to now, single heating rate methods [52–58, 62, 63] have been far more popular than the methods that use several heating rates [51, 59–61] for kinetic evaluations.

The advantages of the non-isothermal experimental technique are at least partially offset by serious computational difficulties associated with the kinetic analysis. The kinetic methods can be conventionally divided into differential and integral methods. Differential methods [50–52, 56, 58, 59, 62, 63] use various rearrangements of equation (1). These methods require values of $d\alpha/dT$ and can be conveniently applied to the data of DTA and DSC experiments; they can also be used with TG data if they are pre-processed by differentiation with respect to time or temperature. Unfortunately, numerical differentiation is usually undesirable because it produces very noisy data. To handle TG data, one should use integral methods [53–55, 57, 60, 61] that originate from the various ways of integrating equation (1). Expanding equation (1) to the conditions of a constant heating rate results in

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E}{RT}\right) dT = \frac{A}{\beta} I(E, T) \quad (7)$$

where the temperature integral, $I(E, T)$, does not have an analytical solution. The problem of the temperature integral has been extensively explored by many workers who have suggested a large variety of approximations which may be found in [21, 22]. The history of the problem, as well as an assessment of the various approximations, have been recently given by Flynn [47]. Prior to the widespread use of personal computers, the development of simple approximations of the temperature integral played an essential role in accurate evaluations of Arrhenius parameters. Nowadays, one can determine Arrhenius parameters by using methods based on numerical integration of equation (7) [64–66].

By the early 1970s a number of studies had been conducted to test whether non-isothermal techniques were capable of producing Arrhenius parameters consistent with the values derived from isothermal experiments. Since isothermal kinetics had been methodologically well established, they were considered to be the standard that non-isothermal kinetics methods had to match. Therefore, non-isothermal Arrhenius parameters were expected to agree with the isothermal values, but not the other way around. Some workers reported reasonable agreement between the Arrhenius parameters estimated from isothermal and non-isothermal measurements [67–70], but in a number of other cases the values were reported to be inconsistent [71–76]. These disagreements were often considered to provide evidence that non-isothermal kinetics methods were invalid. Here, we have to stress that the expectation of close agreement was inspired more by psychological than logical reasons. We will show later that generally one cannot expect Arrhenius parameters derived from isothermal and non-isothermal experiments to be identical.

The notorious work of McCallum and Tanner [77] tried to give a theoretical explanation for inconsistencies in the values of Arrhenius parameters derived from isothermal and non-isothermal experiments. They claimed that use of the differential

rate expression, equation (1), is inappropriate for non-isothermal conditions. Their argument takes the following route. First, the extent of reaction α is written as a function of time and temperature,

$$d\alpha = \left(\frac{\partial\alpha}{\partial t}\right)_T dt + \left(\frac{\partial\alpha}{\partial T}\right)_t dT. \quad (8)$$

In a non-isothermal experiment the temperature is a function of time only, so we can rewrite equation (8) in the rearranged form

$$\frac{d\alpha}{dt} = \left(\frac{\partial\alpha}{\partial t}\right)_T + \beta \left(\frac{\partial\alpha}{\partial T}\right)_t. \quad (9)$$

This equation implies that the reaction rate (and therefore the kinetic parameters) are dependent on the heating rate in the experiment. That is, the 'true' Arrhenius parameters can only be determined by extrapolating the results to infinitely slow heating rates (isothermal conditions). The original hypothesis has been effectively refuted by numerous arguments (see [22] and related references therein). One of the most compelling arguments is that α is not a state function, because its value depends on the path taken to a particular combination of T and t . Therefore, equation (8) cannot be written as an exact differential. Even if equation (8) is considered to be valid for a limited set of conditions, it is instructive to consider the contributions of each of its terms. The first term represents the kinetic contribution to the reaction rate, whereas the second represents a static or thermodynamic contribution. For a solid, one may generally vary the temperature without affecting the amount of the substance present in the solid phase, except if a phase transition (e.g. melting or sublimation) is encountered. Therefore, the second term in equation (8) is normally zero and the apparent dependence on the heating rate vanishes except under very special conditions. The conclusion of many arguments [22] is that there is no fundamental contradiction between kinetic parameters determined from isothermal and non-isothermal experiments. However, the practical problem of inconsistency between Arrhenius parameters derived from isothermal and non-isothermal experiments still persists. This review surveys the problem and its possible solutions.

Our intention is to consider two major reasons (formal and experimental) for the above inconsistency. A formal reason for the inconsistency of Arrhenius parameters derived from isothermal and non-isothermal experiments originates from the commonly used procedure of force fitting experimental data to different reaction models. An experimental reason is that isothermal and non-isothermal experiments are necessarily conducted in different temperature regions, but solid state processes ordinarily show multi-step kinetics that readily change with temperature.

2. Model fitting approach in isothermal and non-isothermal kinetics

It is traditionally expected that kinetic analysis produces an adequate kinetic description of the process in terms of the reaction model and Arrhenius parameters. These three components ($f(\alpha)$, E and $\ln A$) are sometimes called the 'kinetic triplet'. While Maciejewski [78, 79] questioned the very possibility of mechanistically interpreting experimentally found reaction models, determination of these models is often expected to help in elucidating the reaction mechanism. For example, if $f(\alpha)$ is found to follow a first-order rate law, this could be used to support a mechanism in which the rate limiting step is unimolecular. Arrhenius parameters are needed to

Table 2. Arrhenius parameters for isothermal decomposition of ADN.

Model ^a	E (kJ mol ⁻¹)	$\ln A$ (min ⁻¹)	$-r$
1	126.0	26.3	0.9949
2	126.1	26.6	0.9950
3	126.4	26.9	0.9952
4	127.7	27.6	0.9960
5	128.2	27.7	0.9963
6	129.5	29.2	0.9965
7	127.4	27.3	0.9956
8	127.6	27.6	0.9958
9	128.1	28.1	0.9960
10	130.3	27.4	0.9968
11	128.4	27.4	0.9962
12	128.1	27.5	0.9961

^a Enumeration of the models is given in table 1.

describe adequately the temperature dependence of the reaction rate. The whole kinetic triplet is used to predict the reaction rates under various temperature conditions. The predictions have a great practical value in solving a variety of problems such as shelf-life and/or life-time evaluations [80–90]. These evaluations are done by rearranging equation (4)

$$t = \frac{g(\alpha)}{A \exp(-E/RT)}. \quad (10)$$

To determine Arrhenius parameters by equation (1), one has to separate the temperature $k(T)$ and conversion dependence $f(\alpha)$ of the reaction rate. The most popular procedure is force fitting experimental data to different reaction models. Henceforth, this procedure will be referred to as the ‘model fitting method’. Following this method, the $k(T)$ term is determined by the form of $f(\alpha)$ chosen. In isothermal kinetics, these terms are separated by the very conditions of the experiment ($k(T) = \text{constant}$ at constant T). The determination of the $f(\alpha)$ term is achieved by fitting various reaction models (table 1) to experimental data. After $f(\alpha)$ term has been established for a series of temperatures, $k(T)$ can be evaluated. It is important to note that this procedure involves two sequential constrained fits. The first fit finds $f(\alpha)$ from data obtained at constant temperature. The second fit finds E and A based on a fixed form of $f(\alpha)$.

On the other hand, a single non-isothermal experiment provides information on both $k(T)$ and $f(\alpha)$, but not in a separated form. The model fitting method attempts to determine all three members of the kinetic triplet simultaneously. For this reason, almost any $f(\alpha)$ can satisfactorily fit data at the cost of dramatic variations in the Arrhenius parameters which compensate for the difference between the assumed form of $f(\alpha)$ and the true but unknown kinetic model.

Let us compare the results of the model fitting method as applied to both isothermal and non-isothermal data [91] for the thermal decomposition of ammonium dinitramide (ADN). For isothermal data, $k(T)$ can be easily determined by

$$g_j(\alpha) = k_j(T) t \quad (11)$$

for any reaction model. The subscript j has been introduced to emphasize that substituting a particular reaction model into equation (11) results in evaluating the

Table 3. Arrhenius parameters for non-isothermal decomposition of ADN at 5.5 °C min⁻¹

Model ^a	<i>E</i> (kJ mol ⁻¹)	ln <i>A</i> (min ⁻¹)	- <i>r</i>
1	24.5	3.9	0.9783
2	35.1	6.9	0.9813
3	56.2	12.7	0.9837
4	182.9	46.2	0.9862
5	246.2	62.8	0.9865
6	139.4	35.7	0.9928 ^b
7	29.5	5.3	0.9903
8	41.7	9.0	0.9913
9	66.1	15.9	0.9921 ^b
10	269.1	67.4	0.9928 ^b
11	131.0	32.0	0.9924 ^b
12	127.6	31.3	0.9910

^a Enumeration of the models is given in table 1.

^b One of the four best, statistically equivalent models.

corresponding rate constant, which is found from the slope of a plot of $g_f(\alpha)$ versus t . For each reaction model selected, the rate constants are evaluated at several temperatures, T_i , and the Arrhenius parameters are evaluated in the usual manner using the Arrhenius equation in its logarithmic form:

$$\ln k_f(T_i) = \ln A_j - E_j/RT_i. \quad (12)$$

Arrhenius parameters evaluated for the isothermal experimental data by the model fitting method are presented in table 2.

For non-isothermal data, one can use the Coats–Redfern equation [57]

$$\ln [g_f(\alpha)/T^2] = \ln [(A_j R / \beta E_j) (1 - 2RT'/E_j)] - E_j/RT \quad (13)$$

where T' is the mean experimental temperature. This method is reported [92] to be one of the most frequently used to process non-isothermal data. Inserting various $g_f(\alpha)$ into equation (13) results in a set of Arrhenius parameters. The Arrhenius parameters determined from the non-isothermal experimental data on ADN using this method are presented in table 3.

Examination of table 2 shows that the Arrhenius parameters determined for the isothermal data using the model fitting method are almost independent of the reaction model used. In contrast, the Arrhenius parameters obtained for non-isothermal decomposition of ADN are highly variable, exhibiting a strong dependence on the reaction model chosen (table 3). The reason for the failure of the model fitting method applied to non-isothermal data is clear. Unlike isothermal experiments, in which temperature is isolated as an experimental variable, non-isothermal experiments allow fits that vary the temperature sensitivity (E , $\ln A$) and reaction model $f(\alpha)$ simultaneously. A mathematical aspect of the problem has been considered elsewhere [93]. This extra flexibility in the fitting procedure allows errors in the functional form of the reaction model to be concealed by making compensating errors in the Arrhenius parameters, sometimes by as much as one order of magnitude [94–100], which is an unusually large range in comparison to most isothermal experiments [101–104]. Because the model fitting method gives highly uncertain Arrhenius parameters for non-isothermal data, they cannot be used to make a meaningful comparison with the parameters obtained from isothermal data.

Various methods can be used to reduce the above ambiguity. The central idea of all these methods is to formulate a certain principle that allows one to choose an adequate kinetic description from a set of several kinetic triplets. It is important to realize that all these principles are based on information that, by its origin, is extrinsic and therefore may be irrelevant to the particular process being studied.

2.1. Statistical methods

When it comes to choosing a unique kinetic triplet, statistical methods are used in the majority of cases. These methods are based on the idea that an adequate kinetic triplet should be the best statistical description of experimental data. In other words, the adequacy of kinetic description is judged by the goodness of model fitting.

The correlation coefficient r and residual sum of squares s^2 are the values most commonly used to characterize the goodness of fit. The minimum value of the residual sum of squares and/or the maximum absolute value of the correlation coefficient are used to choose the unique kinetic triplet. Unfortunately, in many cases [98–100, 105–108] it is forgotten that these statistical measures are random, and their uncertainties must be taken into account as confidence limits [109]. Therefore, the sole value of the maximum of $|r|$ and/or of the minimum of s^2 is not sufficient for selecting one single kinetic triplet to the exclusion of all others. To rightfully discriminate the kinetic triplets, it is necessary to take into account the confidence limits for the best (i.e. minimum or maximum) statistical characteristics [109–111]. One can discriminate only those kinetic triplets that are characterized by $|r|$ and/or s^2 values that lie outside these confidence limits. All other kinetic triplets are statistically indistinguishable.

For instance, statistical analysis [109] of the linear correlation coefficients (r in table 3) can identify the four ‘best’ reaction models, which in this example are statistically equivalent. Although model 11 (the contracting sphere) is one of the four best, there is nothing about the model fitting analysis to indicate that it is any better or worse than the other three ‘best-fit’ models (models 6, 9 or 10). The four models describe qualitatively different mechanisms, and the corresponding Arrhenius parameters span a factor of four in E and $\ln A$.

The problem of ambiguity in choosing the reaction model also exists in isothermal kinetics [103, 104, 112–115]. However, in this case proper choice of the reaction model does not seem to be vitally important for evaluation of Arrhenius parameters, because they usually do not show a strong dependence on the reaction model. Criado *et al.* [116] offered a theoretical explanation for this effect. Nevertheless, we cannot ignore a few isothermal studies in which the activation energy was reported to vary markedly (43–129 kJ mol⁻¹ [117], 61–183 kJ mol⁻¹ [118], and 26–57 kJ mol⁻¹ [119]) with the reaction model.

2.2. Statistical nonsense

Even if the statistical analysis is performed correctly, it has one very serious flaw that can be exemplified as follows. Suppose we want to establish a dependence between volume V and pressure P for a constant amount n of a gas at a constant temperature T . By plotting the results of a series of the measurements as V_i versus P_i we would observe a nonlinear dependence that follows Boyle’s law, i.e. $V = a/P$. Then, the results of our experiments can be fitted by the least-squares method to an incomplete hyperbolic model, $Y = b/X$, where $Y = V$, $X = P$ and $b = a$. However, if model fitting is to be done by someone who is not aware of the nature of our measurements, a practically countless number of fitting functions could be used, including the general

form of a hyperbolic function, $Y = c/(X - d) + f$. Now the question is, which of the two hyperbolic forms would give a better statistical fit? Most likely this would be the general hyperbolic function that has two additional adjustable parameters and, therefore, is more flexible (e.g. capable of accounting for non-ideal behaviour). However, if we compare the two models from a physical point of view, the parameter b in the incomplete model has a clear physical meaning of the product nRT , whereas parameters c , d , and f of the better statistical description have no physical meaning at all. Needless to say, the same applies to parameters of any other alternative mathematical function no matter how statistically perfect the fit is. This simplistic example shows that the capability of a mathematical model to produce a meaningful information cannot be characterized by the goodness of fit.

2.3. Non-statistical methods

There is a group of infrequently used methods that use some theoretical ideas to facilitate choice of the kinetic model. One such idea is to use the predictions of activated complex theory for the value of the pre-exponential factor. According to this approach, one must choose a reaction model that gives rise to a value of the pre-exponential factor that is in agreement with the vibrational frequency of the activated complex. Not even questioning the theoretical interpretability of experimentally determined effective values of the pre-exponential factor, we have to stress that Cordes [43] gave a rather wide range of values (10^6 – 10^{18} s⁻¹) applicable to solid state reactions. For instance, in table 3 three models (6, 11 and 12) show pre-exponential factors that fit into this interval. The problem of the ambiguous choice of model was also faced by other workers, who used even narrower intervals, 10^{12} – 10^{14} s⁻¹ [120] and 10^{11} – 10^{15} s⁻¹ [121].

Tang and Chaudhri [122] proposed choice of the reaction model from a single isothermal experiment with the chosen model then used for evaluating Arrhenius parameters from non-isothermal data. The method is based on the hypothesis that under both isothermal and non-isothermal conditions a process obeys the same reaction model. It should be remembered, however, that in isothermal kinetics the choice of the reaction model often happens to be ambiguous [103, 104, 112–115]. When applied to non-isothermal data, the rival reaction models would most likely give rise to significantly different sets of Arrhenius parameters.

Gao *et al.* [123] developed a method of choosing reaction models for non-isothermal data based on the fact that, for different reaction models, the extent of reaction at maximum reaction rate α_{\max} falls into a narrow specific range. However, for some of the reaction models these ranges overlap or even coincide. This overlap is a potential source of ambiguity of choosing the reaction models. For example, the non-isothermal decomposition of ADN (table 3) shows the maximum rate at $\alpha_{\max} = 0.67$. According to Gao *et al.* this value is characteristic of two reaction models (models 10 and 11, see table 1). These obviously correspond to two absolutely different reaction mechanisms and give rise to significantly different sets of Arrhenius parameters.

Although there are other non-statistical methods, we feel that instead of discussing these it would be more beneficial to consider general flaws of the model fitting approach.

2.4. What if the reaction model happens to be chosen unambiguously?

In previous sections we have tried to show that an unambiguous choice of reaction model is rather an unlikely outcome of model fitting kinetic analysis. However, let us now suppose that the reaction model has been chosen unambiguously. There are several problems to be considered in this situation.

Firstly, we can never be sure that the unambiguous choice is actually unambiguous. The reaction model is chosen from the list of arbitrarily (subjectively) compiled models. No matter how comprehensive this list may seem, there is absolutely no guarantee that the adequate model is included in the list. For the particular process under study, the adequate model may be yet invented. However, any arbitrarily compiled list always contains a model that gives a better description of the process than do other models in the list. Therefore, even an unambiguous choice still can be wrong and yield an inadequate kinetic triplet. The problem of compiling a complete list of reaction models can be avoided when using the empirical model of Sestak and Berggren [124]

$$f(\alpha) = \alpha^m(1 - \alpha)^n[-\ln(1 - \alpha)]^p \quad (14)$$

where the parameters m , n and p are to be determined as the result of model fitting. The use of equation (14) presents difficulties of both practical and theoretical nature. Practically, the parameters of this equation are difficult to determine reliably because of their strong inter-correlation [125–127]. Theoretically, a rational mechanistic interpretation of equation (14) is possible only for a limited combination of m , n and p [124, 128].

Secondly, even an unambiguously chosen reaction model cannot help in drawing an unambiguous mechanistic conclusion because of the ambiguous association of the kinetic equation with the mechanistic model of a process. Jacobs and Tompkins [129] emphasized that *a posteriori* agreement between the theoretical rate equations and experimental results does not necessarily confirm the basis on which these equations are derived. This statement is rather obvious if we take into account the fact that the same equation can be derived for totally different mechanistic models and the same mechanistic model can give rise to several different equations [130]. For instance, Pysiak [131] demonstrated that the equation of a contracting sphere can be derived from three different mechanistic concepts.

Thirdly, even if a reaction model is unambiguously chosen, Arrhenius parameters may inadequately reflect the temperature dependence of the reaction rate of the process. Solid state reactions ordinarily demonstrate a tangled interplay of various chemical and physical processes such as solid state decomposition, reaction of gaseous products with the solid, sublimation, polymorphous transitions, diffusion, melting, evaporation, adsorption, desorption, etc. Therefore, the effective activation energy of a solid state reaction is generally a composite value determined by the activation energies of various processes as well as by the relative contributions of these processes to the overall reaction rate. Therefore, the effective activation energy is generally a function of temperature. Furthermore, even if the temperature is kept constant (single isothermal experiment), the relative contributions of the elementary steps to the overall reaction rate vary with the extent of conversion, ultimately resulting in a dependence of the effective activation energy on the extent of conversion [91]. Additionally, the kinetics of solid state reactions are known [132] to be sensitive to pressure, size of crystals, gaseous atmosphere and many other factors which are likely to change during the process. Model fitting methods are designed to extract a single set

of global Arrhenius parameters for the whole process, and are therefore unable to reveal this type of complexity in solid state reactions. The values obtained in such a way are in fact averages that do not reflect changes in the mechanism and kinetics with the temperature and the extent of conversion [91].

It should be emphasized that all these problems are peculiar to the model fitting method itself, regardless of whether it is applied to isothermal or non-isothermal data. In a non-isothermal experiment, the temperature and conversion contributions of the reaction rate are not separated, and this strongly aggravates the ambiguity problem. That is why the problem of ambiguity is often considered to be a problem of non-isothermal kinetics, but not a problem of the model fitting approach. Unfortunately, this flawed approach has been employed in an overwhelming majority of kinetic analyses, the failures of which sometimes come to light in a quite bizarre form, such as negative [133] or close to zero [134, 135] values of the activation energy, negative values of the activation entropy for endothermic processes [134, 136, 137], or negative estimated number of collisions [138]. The flood of inconsistent information produced from non-isothermal data with the model fitting method provoked an antagonistic attitude towards non-isothermal kinetics as a whole [21, 139]. In our view this attitude is justifiable only as it pertains to the use of the model fitting approach to kinetic analyses.

In our opinion, the model fitting approach is a rather ineffective way for the kinetic analysis of data. Irrespective of whether the data are isothermal or non-isothermal, the experimentally determined reaction model cannot be unequivocally interpreted in terms of reaction mechanism. The application of the model fitting technique to isothermal data may give rise to consistent values of the Arrhenius parameters. However, the fact that only a single, global kinetic triplet is derived may conceal the existence of complex (e.g. multi-step) kinetics. Model fitting kinetic analysis applied to non-isothermal data produces Arrhenius parameters that are so uncertain that they cannot be meaningfully compared with isothermal values. Furthermore, the ambiguity of the kinetic triplet (or any of its components) does not allow for reliable predictions of the reaction rates [140]. At the present time, the only viable alternative is a model-free approach [141] to kinetic analysis.

3. Model-free approach to reconciliation of isothermal and non-isothermal kinetics

3.1. Isoconversional methods

The model-free approach to kinetic analysis rests upon the isoconversional principle, according to which the reaction rate at a constant extent of conversion is only a function of temperature

$$\left(\frac{d \ln (d\alpha/dt)}{dT^{-1}} \right)_{\alpha} = - E_{\alpha}/R. \quad (15)$$

(Henceforth, the subscript α designates the values related to a given value of conversion.) This principle is the basis of so-called isoconversional methods. As already mentioned, Kujirai and Akahira [37] were the first to propose an empirical isoconversional equation (equation (3)) to evaluate the temperature sensitivity of materials decomposed under isothermal conditions. Later on, the authentic isoconversional equation (equation (5)) was successfully used for analysis of isothermal data [142, 143].

In non-isothermal kinetics, several isoconversional methods were suggested in the

1960s [59–61]. To use these methods, a series of experiments has to be conducted at different heating rates. The isoconversional method suggested by Friedman [59] combines equations (1), (2) and (6) into a linear equation

$$\ln[\beta_i(d\alpha/dT)_{\alpha,i}] = \ln[Af(\alpha)] - E_{\alpha}/RT_{\alpha,i}. \quad (16)$$

(Henceforth, the subscript i represents an ordinal number of the experiment conducted at the heating rate β_i .) The methods of Ozawa [60] and Flynn and Wall [61] use approximations of the integral form of equation (7). The use of Doyle's approximation [144] of the temperature integral in equation (7) yields

$$\ln(\beta_i) = \text{constant} - E_{\alpha}/RT_{\alpha,i}, \quad (17)$$

which is used in the isoconversional methods of Ozawa and of Flynn and Wall for evaluating the activation energy. For smaller E/RT , equation (17) needs a correction for E [145]. In our view, the method of Kissinger [51], that employs the equation

$$\ln(\beta_i/T_{m,i}^2) = \text{constant} - E/RT_{m,i}, \quad (18)$$

cannot be rightfully grouped with the isoconversional methods because the value of T_m (the sample temperature at which peak differential thermal analysis deflection occurs) used in this method corresponds to an extent of conversion that varies with the heating rate [122].

To avoid inaccuracies associated with analytical approximations of the temperature integral, Vyazovkin [65, 66] proposed a nonlinear isoconversional method. According to this method, for a set of n experiments carried out at different heating rates, the activation energy can be determined at any particular value of α by finding the value of E_{α} for which the function

$$\sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_{\alpha}, T_{\alpha,i}) \beta_i}{I(E_{\alpha}, T_{\alpha,j}) \beta_j} \quad (19)$$

is a minimum.

A model-free estimate of the activation energy can also be obtained from a single experiment by the temperature jump method [12, 146] in which the sample temperature at a certain moment is quickly changed to another value. This method assumes that the extent of conversion does not vary during the temperature jump, i.e. the change in the reaction rate is proportional to the rate constant alone. Under this assumption, which may hold only if the reaction rate is not too high, one can obtain a model-independent estimate of the activation energy, which obviously corresponds to a given extent of conversion α . In fact, the temperature jump method is an experimental realization of the isoconversional principle. The temperature jump method was proposed [147] for use in kinetic computations in controlled rate thermal analysis (CRTA) [148]. CRTA experiments are usually performed at low reaction rates which are kept constant by continuously adjusting the sample temperature.

Three to five experiments are performed usually to estimate Arrhenius parameters by equations (16) and (17). The use of both small population and linearization in (16) and (17) invalidates the implementation of the statistical procedures based on the normal distribution. Vyazovkin and Sbirrazzuoli [149] showed that in the case of estimating the activation energy by the isoconversional method, Student's confidence intervals happen to be excessive. A comparison with confidence intervals estimated by a non-parametric (distribution-free) method has allowed for correcting Student's percentiles [149].

3.2. Problems associated with the application of isoconversional methods

There are several problems that seem to hamper extensive use of isoconversional methods. Firstly, the original isoconversional methods (e.g. Friedman [59], Ozawa [60] and Flynn and Wall [61]) do not suggest a direct way of evaluating either the pre-exponential factor or the reaction model. Several procedures [150–153] have been proposed to determine these two components when using model-free techniques. Flynn [153] suggested assuming that a reaction obeys a reaction order model, $f(\alpha) = (1 - \alpha)^n$. Then, at $\alpha \approx 0$ the intercept of a plot of equation (16) gives $\ln A$. Once $\ln A$ is known, one can determine n by plotting $\ln [f(\alpha)]$ versus α [153]. Malek [152] proposed parameterizing the product $Af(\alpha)$ in terms of the Sestak–Berggren equation (14). A very similar procedure was suggested earlier by Gontkovskaya *et al.* [151]. We have already noted that this approach has the disadvantage that the parameters m , n and p of equation (14) are strongly inter-correlated.

As we can see all these methods require the assumption of a certain form of the reaction model and consequently the resulting estimates of the pre-exponential factor are model-dependent. The only model-free way for evaluating the pre-exponential factor has been proposed by Vyazovkin and Lesnikovich [150]. This procedure makes use of the so-called ‘compensation effect’ that manifests itself as a linear correlation of Arrhenius parameters evaluated for the same process when using different reaction models (e.g. see table 3)

$$\ln A_j = c + dE_j \quad (20)$$

(where j specifies each reaction model e.g. 1–12). Once the correlation parameters c and d have been evaluated, the E_α values are substituted for E_j in equation (20) to estimate the corresponding $\ln A_\alpha$ values. Vyazovkin and Linert [154] showed that this method can be used to estimate the pre-exponential factors of multi-step reactions.

Having determined the values of the pre-exponential factor and the activation energy, one can reconstruct the reaction model numerically [141, 155]. The integral form of the reaction model, $g(\alpha)$, can be reconstructed by substituting model-independent estimates of E_α and A_α into equation (7). Alternatively, the differential form of the reaction model, $f(\alpha)$, can be reconstructed using the expression

$$f(\alpha) = \frac{\beta(d\alpha/dT)_\alpha}{A_\alpha \exp(-E_\alpha/RT_\alpha)} \quad (21)$$

An explicit form of the reaction model can then be identified by comparing proposed models (e.g. those in table 1) to the numerically determined reaction model $f(\alpha)$ or its integrated form $g(\alpha)$. It is apparent that any meaningful interpretation of such a reconstructed reaction model can be attempted only for a single-step process. An indication of this situation might be if E_α were found to be independent of α . The same requirement applies equally to the methods mentioned earlier in this section.

The most serious problem with the use of isoconversional methods, however, is that variation of the Arrhenius parameters with the extent of reaction poses difficulties in the interpretation of the kinetic data. For instance, Agrawal [156] claims that for multi-step reactions the isoconversional method of Friedman yields meaningless values of the activation energy. Schneider [157] observed systematic variations of Arrhenius parameters with α for the thermal decomposition of various polymers. Based on this fact, it was concluded that Arrhenius parameters cannot be used either for elucidating the reaction mechanism or for predicting the reaction rates.

Nevertheless, let us dwell briefly on this problem. The problem of interpretation of the dependence of E_α on α comes from the theoretical concepts that prescribe the activation energy of an elementary reaction step to be constant in gases and in dilute solutions. However, as mentioned above, the effective activation energy of a solid state reaction is generally a composite value determined by the activation energies of various elementary processes. We must therefore accept the fact that E_α may vary with α , and abandon the notion that a single activation energy controls the temperature dependence of the reaction rate throughout the entire duration of a solid state reaction.

Variation of the activation energy with the extent of conversion was originally observed by Flynn and Wall [61] who applied an isoconversional method to synthetic non-isothermal data on multi-step kinetics. Elder [158–162] and Dowdy [163, 164] conducted systematic studies of isoconversional methods as applied to complex processes comprising competing or independent reactions; both workers concluded that the methods are applicable to the study of multi-step processes. Dowdy [164] noticed that the application of differential (equation (16)) and integral (equation (17)) methods to the same multi-step kinetics results in somewhat different E_α dependencies. This happens because the approximation of the temperature integrals employed in equation (17) is obtained under the assumption of constant E . Violation of this assumption for multi-step kinetics makes the activation energy deviate from the actual value. For systems of two competing and/or two independent reactions with activation energies of 167 and 251 kJ mol⁻¹, Dowdy [164] found these deviations to be less than 4%. Therefore, for processes that show a moderate variation of E with α , we may generally expect the deviations to be within the conventionally accepted 10% level of error in the activation energy. Nevertheless, there are two ways to avoid these deviations. Firstly, one can use the differential isoconversional method (equation (16)) that works well for differential type experimental data such as DSC or DTA data. For TG data, one must resort to numerical differentiation, which pollutes the data with a significant amount of noise. Unfortunately, Friedman's method (as well as other differential methods) shows markedly lower resistance to noise that may result in erroneous values of the activation energy [165, 166]. Another solution of the problem is to carry out the temperature integral (equation (7)) with E as a function of T . This procedure can be realized within the nonlinear isoconversional method [65, 66] (equation (19)).

Vyazovkin and Lesnikovich [167] showed that revealing the dependence of the activation energy on conversion not only helps to disclose the complexity of a process, but also helps to identify its kinetic scheme. The shapes of the dependence of E_α on α have been identified from simulated data for competing [167], independent [168], consecutive [169] and reversible [170] reactions, as well as for reactions complicated by diffusion [171]. Principles and examples of the mechanistic interpretations of the dependence of E_α on α can be found elsewhere [141, 167, 172–178].

The occurrence of the dependence of the activation energy on the extent of conversion also creates a problem for predicting the reaction rates. This problem is often overcome by averaging [179–182] E_α over α . Because averaging is only valid when applied to randomly varying values, the averaging of systematic dependencies [179–182] of E_α on α is statistically meaningless. This procedure might be justified when a change in E_α is several per cent of the mean value [179, 180], but not when such a change is comparable to the mean value [181, 182] (cf. the case for ammonium perchlorate considered here in section 3.5).

The problems of using isoconversional methods for kinetic predictions can be resolved without averaging E_α and even without evaluating the reaction model and the pre-exponential factor. To do this we have to assume that the partial (i.e. related to a given conversion) kinetic triplets remain the same under variable temperature. Using this assumption, we can equate equation (4) (isothermal conditions) and equation (7) (non-isothermal conditions) related to a given conversion. Simultaneous solution of these equations for time yields

$$t_\alpha = \frac{\int_0^{T_\alpha} \exp(-E_\alpha/RT) dT}{\beta \exp(-E_\alpha/RT_0)}. \quad (22)$$

This equation enables the time at which a given conversion will be reached at an arbitrary temperature, T_0 , to be computed. Equation (22) was first derived by Vyazovkin and Lesnikovich [183]. Later, similar equations were obtained by Khabenko and Dolmatov [184] and Gimzewski [185]. This assumption of conservation of the partial kinetic triplets also permits one to evaluate the functions $[\alpha(T)]_\beta$, $[\alpha(T)]_\beta$, $[t(T)]_\alpha$, $[T(\beta)]_\alpha$ and $[\alpha(\beta)]_T$ without knowledge of the reaction model or the pre-exponential factor [186].

In our opinion, the E_α dependence is not a curse that afflicts the isoconversional methods, but rather a blessing that makes them a powerful tool for analysis of complex solid state kinetics. Recently we showed that use of the isoconversional method allowed different workers to produce consistent dependencies of the activation energy on the extent of conversion [178]. Now we want to explore an opportunity of using the isoconversional method to obtain consistent kinetic information from isothermal and non-isothermal data. Experimental comparisons of E_α dependencies are performed very infrequently. We can mention a work by Reading *et al.* [187] who used the isoconversional method to study the thermal decomposition of calcium carbonate under isothermal, non-isothermal, and CRTA conditions. In that work, a weak dependence of E_α on α was observed. The averaged values of the activation energy were found to be consistent. Recently, Tanaka *et al.* [97] reported consistent E_α dependencies for the thermal dehydration of lithium sulphate monohydrate.

3.3. Theoretical example

Because comparison of isothermal and non-isothermal results can be marred by uncontrolled experimental factors (such as mass and thermal transport, the temperature jump required to start each isothermal experiment and others) let us first consider an ideal case of synthetic data generated by numerical simulation of a model reaction system. The particular kinetic scheme chosen is two parallel reaction channels



each of which follows Mampel's (first-order) model [31]. This model is the most widely [92] used of the models listed in table 1. The chosen reaction system is appropriate to a mixture of two different solids that react in the same temperature region [188], or the reaction of a substance that exists simultaneously in several interconverting forms [173, 189], or the separate decomposition of different end groups [157]. The model may also be appropriate to a system in which localized melting causes reactions to occur in both the liquid and solid phases [190].

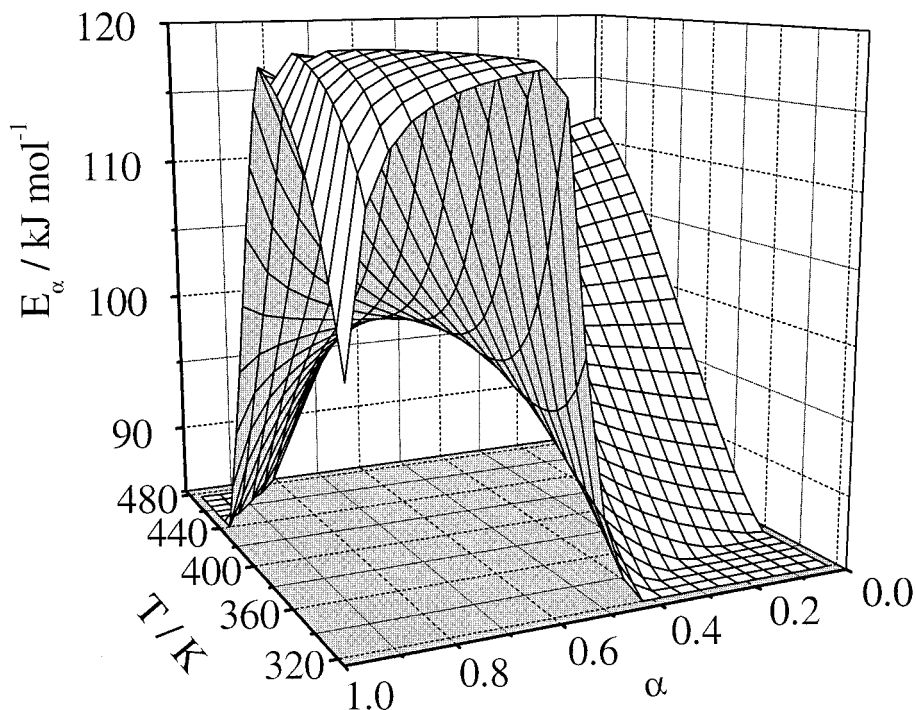


Figure 1. Surface plot of activation energy as a function of extent of conversion and temperature for synthetically generated data under isothermal conditions.

Assuming that the two channels make equal contributions to α , the overall reaction rate is

$$\frac{d\alpha}{dt} = \frac{1}{2} \left(\frac{d\alpha_1}{dt} + \frac{d\alpha_2}{dt} \right) = \frac{1}{2} [k_1(T)(1-\alpha_1) + k_2(T)(1-\alpha_2)]. \quad (24)$$

The effective activation energy of the process is

$$E_\alpha - \left(\frac{d \ln(d\alpha/dt)}{dT^{-1}} \right)_\alpha = \frac{E_1 k_1(T)(1-\alpha_1) + E_2 k_2(T)(1-\alpha_2)}{k_1(T)(1-\alpha_1) + k_2(T)(1-\alpha_2)} \quad (25)$$

which is clearly a function of both temperature and extent of conversion.

The Arrhenius parameters of individual steps were taken to be $A_1 = 10^{10} \text{ min}^{-1}$, $E_1 = 80 \text{ kJ mol}^{-1}$; $A_2 = 10^{15} \text{ min}^{-1}$, $E_2 = 120 \text{ kJ mol}^{-1}$. These values were chosen so that the rates of the two steps are comparable within the working range of temperatures. Isothermal simulations were performed, spanning the range 320 to 480 K in steps of 4 K. At each temperature, we determined the values of α_1 and α_2 corresponding to overall conversions $0.01 \leq \alpha \leq 0.99$ in intervals of 0.02. The values of T , α_1 and α_2 were substituted into equation (25) to plot the effective activation energy as a function of the temperature and overall conversion for isothermal conditions. The results are shown in figure 1.

Non-isothermal simulations were also performed to cover the experimentally practicable range of heating rates from 0.5–100 K min^{-1} . The temperature integral was computed using the approximation of Senum and Yang [191]. At each heating rate, the temperatures were determined corresponding to extents of overall conversion

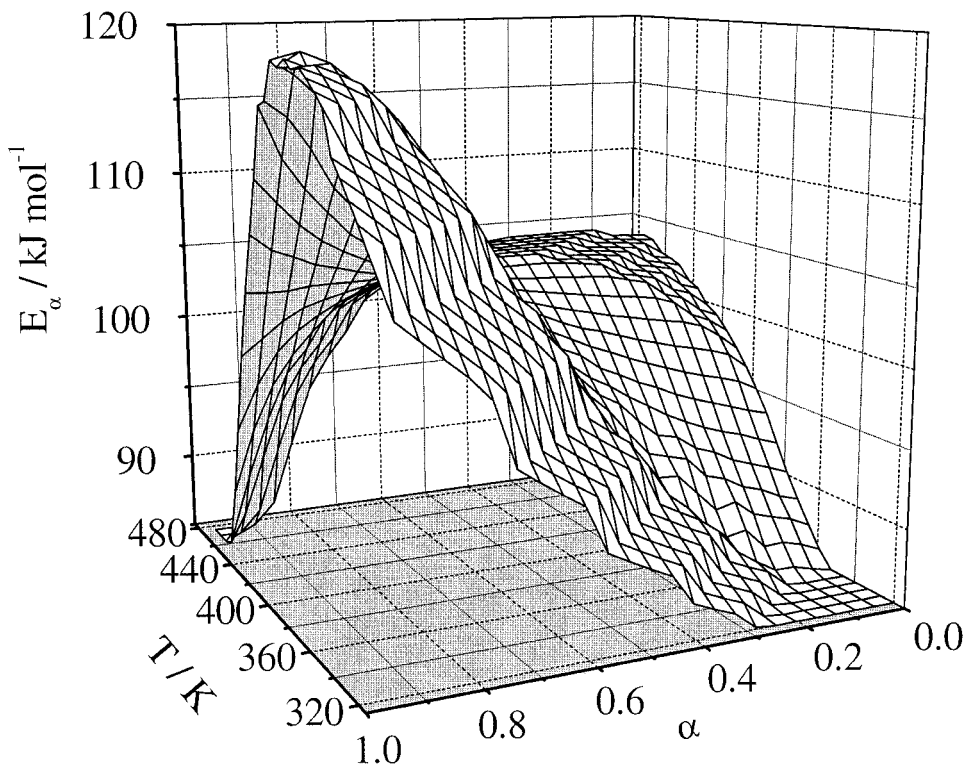


Figure 2. Surface plot of activation energy as a function of extent of conversion and temperature for synthetically generated data under non-isothermal conditions.

$0.01 \leq \alpha \leq 0.99$ in intervals of 0.02. These temperatures and the corresponding partial conversions α_1 and α_2 were inserted into equation (25) to plot the effective activation energy as a function of temperature and overall conversion. The temperature region covered in the non-isothermal simulations was approximately 320 K ($T_{0.01}$ at 0.5 K min^{-1}) to 480 K ($T_{0.99}$ at 100 K min^{-1}). The resulting surface plot of E_α as a function of T and α for non-isothermal simulations is shown in figure 2.

Although the surfaces presented in figures 1 and 2 have some common features (the same locations of minima, rather close locations of the maximum, and the range of variation in E_α), the shapes of the surfaces are different. The root cause of this is that the global extent of conversion α does not uniquely determine the composition of the sample (α_1, α_2). At the same values of α and T , the contributions of the single reaction measured as α_1 and α_2 are respectively different in the isothermal and non-isothermal experiment. This ultimately causes the differently shaped surfaces in figures 1 and 2.

Whereas synthetic data allow E_α to be determined at any single temperature, experimental evaluation of E_α requires several experiments to be performed at different temperatures or heating rates. For this reason, experimentally determined dependencies of E_α on α are always averaged over some temperature interval. The activation energy derived from isothermal experiments is an average over the range of temperatures selected for the experiments, whereas E_α derived from non-isothermal experiments is an average over a variable range of rising temperatures. Therefore, isothermal and non-isothermal experiments not only give rise to different $E(\alpha, T)$ surfaces, but they also cut and average slices of these surfaces in different ways. The

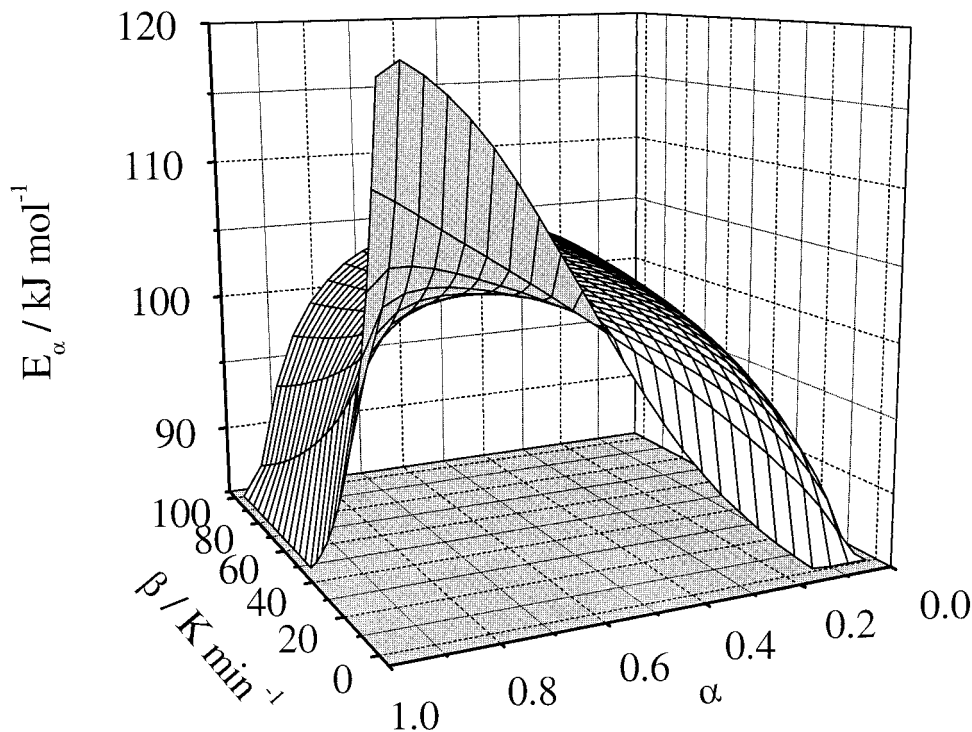


Figure 3. Surface plot of activation energy as a function of extent of conversion and heating rate for synthetically generated data under non-isothermal conditions.

upshot of this is that we may not generally expect the isothermal and non-isothermal dependencies of E_α on α that we observe as the projections of those cuts to be identical. However, because of the aforementioned common features of the isothermal and non-isothermal surfaces, we may expect that under certain conditions the corresponding dependencies of E_α on α will be quite similar. By conducting the experiments over comparable ranges of temperature, we may bring the isothermal and non-isothermal dependencies of E_α on α closer to each other. However, it is difficult to conduct isothermal experiments over a wide range of temperatures. For instance, isothermal experiments can hardly be conducted in the temperature region 320–480 K; the time to completion of the process is about 10 s at 480 K and more than two months at 320 K. A practical temperature region would rather be 360–400 K, with respective times to completion of 1000–20 min. Variation of the heating rate β allows for significant changes in the temperature region of a non-isothermal experiment. An increase of the heating rate from 0.5 to 100 K min⁻¹ makes the temperature region ($T_{0.01} - T_{0.99}$) of the experiment change from 320–400 K to 390–480 K. Variation of the heating rate is thus an effective means of manipulating the dependence of E_α on α . Figure 3 presents the surface of the effective activation energy as a function of α and β . As seen in this figure, the E_α dependencies at slow heating rates (< 10 K min⁻¹) show reasonable similarity to the E_α dependence at the temperatures accessible in isothermal experiments (figure 1).

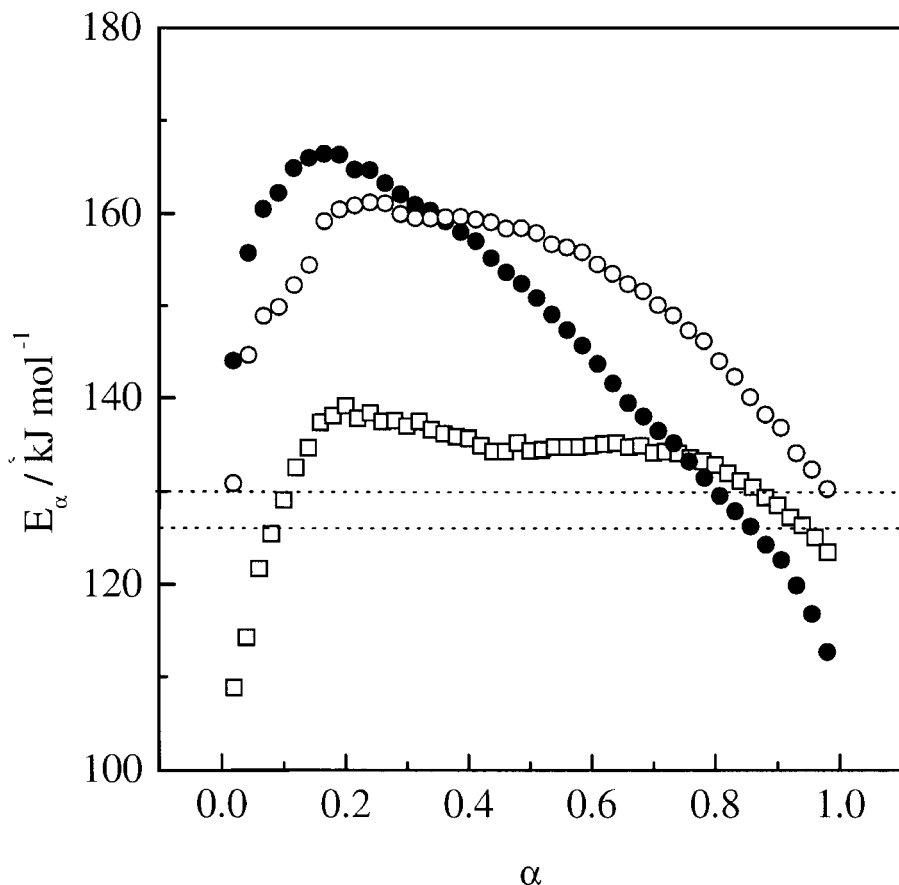


Figure 4. Dependence of the activation energy on extent of conversion determined by the isoconversional method for isothermal (open squares) and non-isothermal (open circles, $\beta = 1.5, 4.0$ and 5.5 °C min⁻¹; full circles $\beta = 1.5, 4.0, 5.5, 8.0$ and 9.5 °C min⁻¹) TG data for the thermal decomposition of ammonium dinitramide. The dashed lines show the limits for the value obtained by the model fitting method from isothermal data.

3.4. Thermal decomposition of ammonium dinitramide

Application of equation (5) to the isothermal data for ADN decomposition permits a determination of E_α as a function of α [91] (open squares in figure 4). The activation energy at low conversion rises from about 110 kJ mol^{-1} at low conversion to nearly 140 kJ mol^{-1} at 20% conversion, and it subsequently decreases to about 124 kJ mol^{-1} near completion of the reaction. Unlike the model fitting method, which yields a single overall value of activation energy for the process ($126\text{--}130 \text{ kJ mol}^{-1}$ depending on the reaction model chosen), the isoconversional technique may reveal a complexity of the reaction mechanism in the form of a functional dependence of the activation energy on the extent of conversion. Because most solid state reactions are not simple one-step processes, analysis of isothermal data by the isoconversional technique is well suited to revealing this type of complexity that might be hidden in a model fitting kinetic analysis (cf. figure 4).

Figure 4 shows the dependence of the activation energy on extent of ADN conversion, as computed by the nonlinear isoconversional method (equation (19)). The dependence is similar in shape to the isothermal case. When all five data sets are

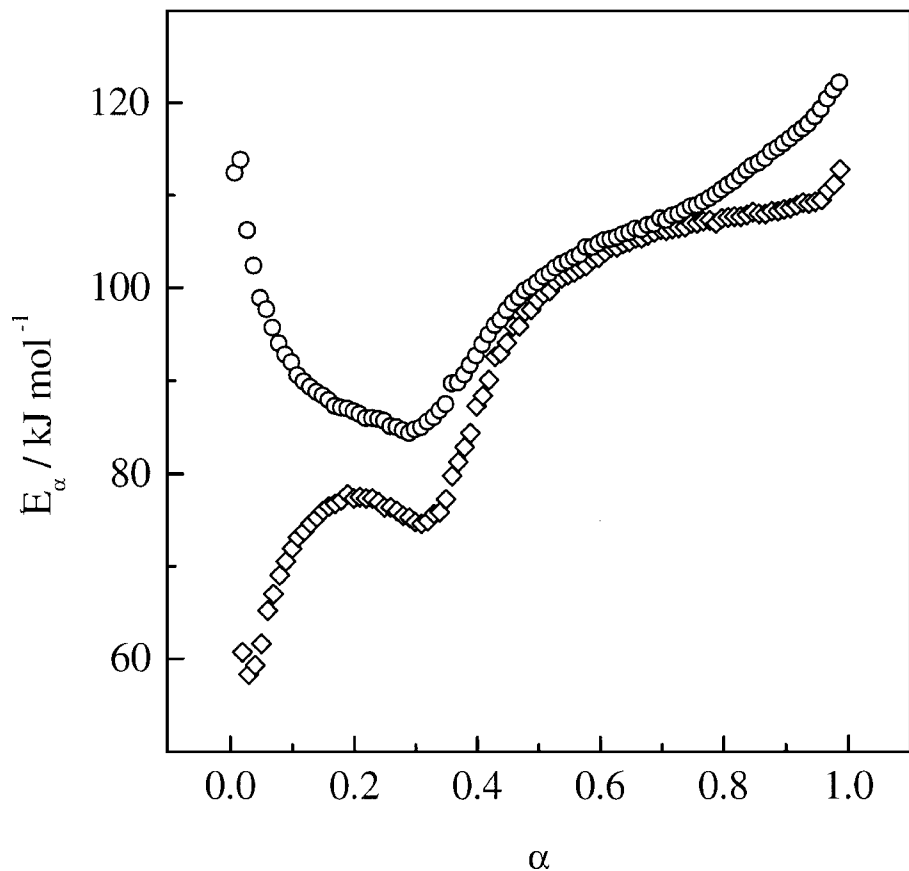
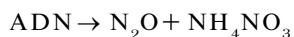
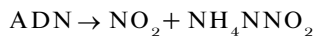


Figure 5. Dependence of the activation energy on the extent of conversion determined by the isoconversional method for isothermal (squares) and non-isothermal (circles) TG data for the thermal decomposition of ammonium perchlorate.

included in the analysis (full circles in figure 4), the activation energy increases to a maximum around 168 kJ mol^{-1} at 17% conversion, then decreases monotonically to 112 kJ mol^{-1} near the end of the reaction. When only the results of the experiments at the three lowest heating rates are included, the variation in E_α is not as dramatic. In our recently published study [177, 192], data from other types of experiments indicated the presence of at least two competing reaction pathways



which could account for the variation in temperature sensitivity during the course of the reaction.

Whereas the isothermal and non-isothermal dependencies of E_α on α have rather similar shapes, their direct comparison should not be made because non-isothermal experiments cover a much wider range of temperatures ($125\text{--}220 \text{ }^\circ\text{C}$) than is practical for isothermal experiments ($132\text{--}150 \text{ }^\circ\text{C}$). The use of slow heating rates allows one to narrow the temperature range of a non-isothermal experiment and this may help to reduce the quantitative difference between the dependencies of E_α on α derived for isothermal and non-isothermal experiments (figure 4).

3.5. Thermal decomposition of ammonium perchlorate

We have also examined the thermal decomposition of ammonium perchlorate (AP) [193]. There is a plethora [194–197] of experimental data on this subject, but very little agreement on the kinetics or mechanisms by which this material decomposes.

The two major steps of the thermal decomposition of AP are mirrored in the dependence of the activation energy on the extent of conversion (figure 5). The first step ($\alpha = 0-0.3$) relates to exothermic decomposition. As the material reacts, it becomes microporous. Then, dissociative sublimation to ammonia and perchloric acid begins to dominate the overall kinetics of gas formation, because the rate of this process is proportional to the surface area. A series of isothermal and non-isothermal TG analysis experiments showed that the reaction becomes more temperature-sensitive (i.e. E_α increases, see figure 5) at $\alpha > 0.3$ as the dissociative vaporization process becomes dominant. The value of E_α corresponding to the maximum temperature (or α) represents the greatest contribution of sublimation to the overall rate of decomposition. The effective value $E_{\alpha=1}$ (125 kJ mol^{-1}) is in good accord with the theoretically and experimentally determined value of Jacobs and Russel-Jones [198].

Whereas at $\alpha > 0.2$ the E_α dependencies are very close for isothermal and non-isothermal experiments, they are completely different near the beginning of the reaction. The interpretation of this behaviour is that different processes limit the global kinetics in the two kinds of experiment. In isothermal experiments, the brief temperature jump to the decomposition temperature limits the time available for nucleation of reactive sites in the crystal, and the global kinetics are limited by the rate of nucleation. In contrast, the temperature rises gradually in non-isothermal experiments, so nucleation occurs over a longer time scale, and the global kinetics are limited by growth of the nucleated sites instead.

3.6. Thermal decomposition of HMX

For the thermal decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), there appears to be a single rate-limiting step in the reaction mechanism, which results in a nearly constant value of the activation energy as a function of the extent of reaction. Figure 6 shows the results of sets of DSC and TG analysis experiments under isothermal and non-isothermal conditions [199]. All of the data were collected for exothermic reaction of HMX at temperatures below its melting point (278°C). The good agreement of the results provides a graphic example of how the isoconversional method of data analysis can give consistent results not only under different experimental conditions (isothermal and non-isothermal), but also for different types of experiments (DSC and TG analysis).

3.7. Epoxy cure

Epoxy cure represents another group of reactions that shows a very complex kinetic behaviour. During the cure, epoxy systems undergo transformation from liquid to gel (gelation) and from gel to glass (vitrification). These transformations profoundly affect the overall kinetics of cure [176]. Sbirrazzuoli [200] has recently applied the isoconversional method to data on the cure of an epoxy anhydride system (diglycidyl ether of bisphenol A and hexahydromethylphthalic anhydride). Figure 7 presents the E_α dependences for the process studied under isothermal and non-isothermal conditions. Although the processes show complex kinetics, the E_α dependences obtained under isothermal and non-isothermal conditions are practically coincident.

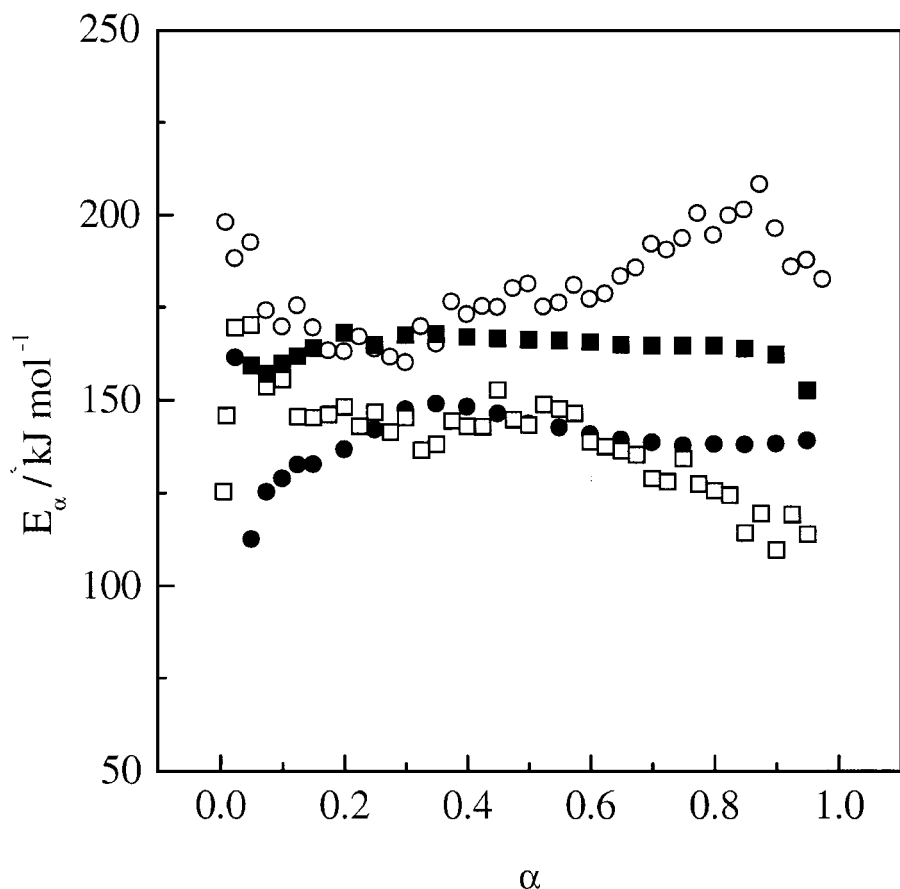


Figure 6. Dependence of the activation energy on the extent of conversion determined by the isoconversional method for isothermal (squares) and non-isothermal (circles) TG (full symbols) and DSC (open symbols) data for the thermal decomposition of HMX.

4. Conclusions

Historical analysis shows that the concepts of solid state kinetics were developed for isothermal processes. The kinetic theory was based on the development of new reaction models that were supposed to relate mechanistic ideas with kinetic observations. The centrepiece of this kinetic methodology was fitting experimental data to reaction models. The model fitting approach is expected to produce information about both the mechanism and the kinetic constants of the process. However, the model fitting approach is inexorably flawed by its inability to determine the reaction model uniquely. Even if the reaction model were unambiguously determined, it could not be uniquely interpreted in terms of a particular reaction mechanism. This is equally true for experiments carried out under isothermal and non-isothermal conditions. The explosive development of non-isothermal kinetics further exposed the model fitting approach as being incapable of producing unambiguous Arrhenius parameters. The latter happen to be so uncertain that they cannot be meaningfully compared with the isothermal values. Resolution of this and many other problems comes in the form of the model-free kinetic analysis based on the isoconversional method. For solid state kinetics, this approach gives rise to an alternative methodology for the kinetic analysis of both isothermal and non-

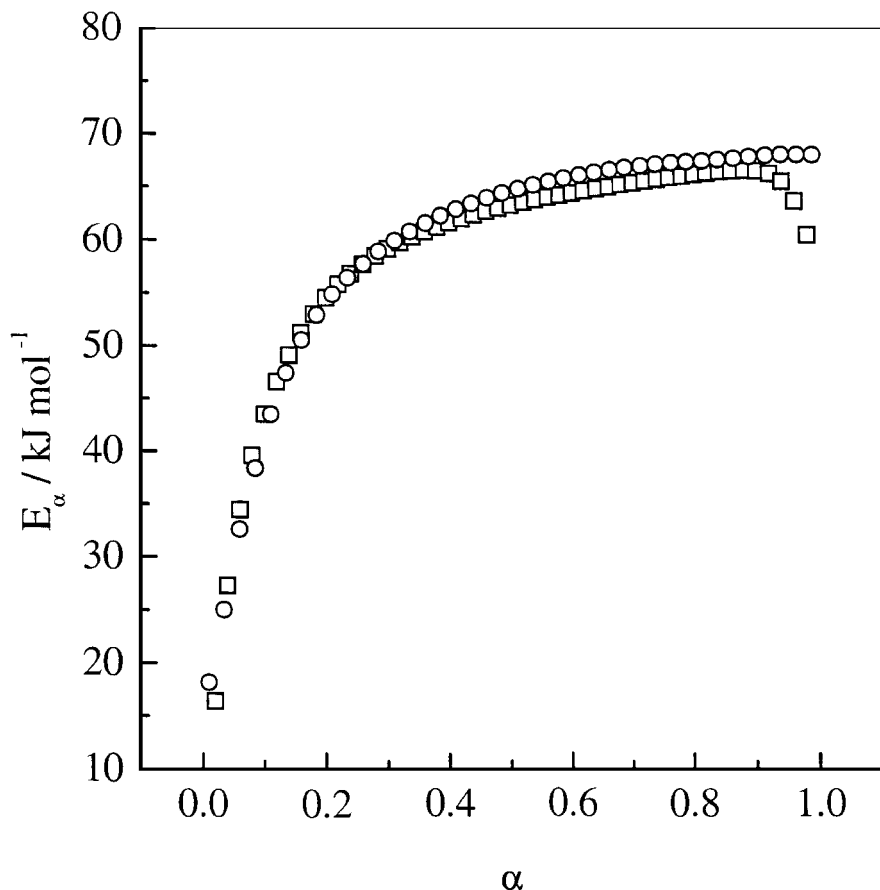


Figure 7. Dependence of the activation energy on the extent of conversion determined by the isoconversional method for isothermal (squares) and non-isothermal (circles) DSC data for the epoxy anhydride cure.

isothermal experimental data. The model-free methodology is built around the dependence of the activation energy on the extent of conversion which is used for both drawing mechanistic conclusions and predicting reaction rates.

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