Evaluation of Activation Energy of Thermally Stimulated Solid-State Reactions under Arbitrary Variation of Temperature

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ABSTRACT

The thermal effect of a reaction makes the temperature inside the reaction system deviate from a prescribed heating program. To take into account the effect of such temperature deviations on kinetic evaluations, a computational method applicable to an arbitrary variation in temperature has been developed. The method combines the isoconversional principle of evaluating the activation energy with numerical integration of the equation, $d\alpha/dt = k[T(t)]f(\alpha)$, over the actual variation of the temperature with the time, $T(t)$. Details of the numerical algorithm are reported. A model example has been used to verify the reliability of this method as compared to an analogous method which does not account for the deviations of the temperature from a prescribed program. The method has been tested for tolerance for noise in the temperature. © 1997 by John Wiley & Sons, Inc.

Introduction

Kinetic studies of thermally stimulated reactions in solids are ordinarily performed under isothermal (temperature is a constant) or linear nonisothermal (temperature is a linear function of the time) heating. Eq. (1)

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

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[where $f(\alpha)$ is the reaction model (Table I), α is the extent of conversion, $k(T)$ is the Arrhenius rate constant, T is the temperature, t is the time, A is the pre-exponential factor, and E is the activation energy] is used[1,2] to describe the kinetics of these reactions under both isothermal and nonisothermal conditions.

If an experimental method measures a physical value proportional to the reaction rate; for example, the heat flow from the reacting system, then eq. (1) can be directly applied to find Arrhenius parameters of the process. If a physical value pro-

TABLE I.
Set of Alternate Reaction Models Applied to Describe Thermal Transformations in Solids.[1,2]

N	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	$1-\alpha$	$-\ln(1-\alpha)$
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	$3/2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
11	Contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$

portional to the extent of conversion (e.g., the mass loss of a substance the pressure, and/or volume of a released gas) is measured, the experimental data need to be numerically differentiated to estimate Arrhenius parameters by eq. (1). However, numerical differentiation considerably lowers the signal-to-noise ratio in experimental data, which makes use of eq. (1) unfavorable for the integral data. Integration of eq. (1):

$$\int_0^\alpha [f(\alpha)]^{-1}\,d\alpha \equiv g(\alpha)$$

$$= A\int_0^t \exp[-E/RT(t)]\,dt \quad (2)$$

[where $g(\alpha)$ is the integral form of the reaction model (Table I) and $T(t)$ is the variation of the temperature during the experiment] provides the basis for methods to evaluate Arrhenius parameters from the integral experimental data. Integral methods are also applicable to differential data subject to their numerical integration. Compared to numerical differentiation, this procedure is more tolerant of the experimental noise. Therefore, integral methods turn out to be more universal than differential ones.

The variation of the temperature during the experiment, $T(t)$, has to be known in order to integrate eq. (2). In the case of isothermal heating, $T(t) = \text{const}$, integration is straightforward. However, the use of a linear heating program, $T(t) = To + \beta t$, leads to the integral, $I(E, T)$, which has no analytical solution:

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

$$= (A/\beta)I(E, T) \quad (3)$$

where β is the heating rate, dT/dt. The problem of integrating eq. (3) is resolved with the help of various approximations[1,2] that enable one to derive convenient equations for evaluating Arrhenius parameters. This problem has also stimulated some theoretical efforts[3] in the field of nonlinear heating programs. It has been particularly shown that hyperbolic[3] as well as parabolic[4] heating programs lead to exact analytical solutions of the temperature integral. Nevertheless, these programs have not gained extensive acceptance.

All of the above heating programs are represented by analytical functions, $T(t)$, which may be called "prescribed heating programs." Whatever the prescribed heating program may be, the actual variation of the temperature inside the reaction system tends to deviate from that prescribed, primarily due to the thermal effects of the reactions. Experimental measurements performed on $CaC_2O_4 \cdot H_2O$ (sample mass 26 mg) and on a mixture of $CaCO_3$ with $Ca(OH)_2$ (sample mass 56 mg) have shown[5] that the endothermic effects accompanying the thermal transformation of these substances make the actual sample temperature deviate from the prescribed linear program ($\beta = 10$ K min^{-1}) by as much as 10 K. Unplanned variations in the temperature obviously affect the reaction kinetics in an unpredictable way and invalidate the use of integral equations based on the assumption that a prescribed heating program holds. Therefore, if integrating eq. (2) does not account for the actual variation of the temperature inside the reaction system, the difference between the prescribed and actual temperature will inevitably result in erroneous values of computed Arrhenius parameters.

The purpose of this article is to develop an integral method to evaluate the activation energy which accounts for an actual variation of the temperature inside the reaction system. According to the isoconversional principle, the reaction rate at a constant conversion depends only on the temperature:

$$d \ln(d\alpha/dt)_\alpha / dT^{-1} = -E_\alpha/R \qquad (4)$$

(here and henceforth the subscript α indicates values related to a given conversion). This principle has been taken as the basis for the method. In this article, great emphasis is given to evaluation of the activation energy throughout the entire interval of conversions. The problem of evaluating both the pre-exponential factor and the reaction model has been deliberately left aside for the following reasons. First, the methods to determine A and $f(\alpha)/g(\alpha)$ have been reported elsewhere.[6] Second, the dependence of the activation energy on conversion seems to have prime importance, because the knowledge of the dependence of E_α on α alone allows one to explore the mechanism and kinetics of a process.[6] For a single-step process, E_α is independent of α and may have the meaning of the intrinsic activation energy. Multistep processes reveal a dependence of E_α on α, the analysis of which helps not only to disclose the complexity of a process but also to identify its kinetic scheme.[6] The sole dependence of the activation energy on conversion is sufficient to predict reliably the behavior of a substance.[6] All these compelling advantages of the isoconversional method have stimulated our efforts to extend the capabilities of the method to conditions that are typical of solid-state reaction systems. An adaptation of the method for an arbitrary variation of temperature is expected to be a major step forward in this direction. The method presented here seems to be the first attempt to adapt an integral isoconversional method to an arbitrary variation of temperature.

Integral Isoconversional Method Applicable to Arbitrary Variation of Temperature

The isoconversional principle has been used in the integral methods of Flynn and Wall[3] and Ozawa.[7] The basic assumption of these methods is that the reaction model, $g(\alpha)$, is independent of the heating rate. Under this assumption $g(\alpha)$ is a constant at a given conversion. Replacing the temperature integral in eq. (3) with the Doyle's approximation[8]:

$$I(E, T) \approx (E/R)\exp(-5.331 - 1.052\,E/RT) \quad (5)$$

one can easily arrive at an equation linear in $T_{\alpha,i}^{-1}$:

$$\ln \beta_i = \ln[\,A_\alpha E_\alpha / g(\alpha) R\,]$$
$$- 5.331 - 1.052\,E_\alpha/RT_{\alpha,i}$$

(where i is an ordinal number representing experiments performed at different heating rates, β_i; and $T_{\alpha,i}$ is the temperature at a given conversion in an experiment performed at β_i) which enables E_α to be evaluated[3,7] from the slope of a plot of $\ln \beta_i$ against $T_{\alpha,i}^{-1}$. Because the approximation (5) holds only for a linear heating program, these plots cannot be used to evaluate E_α in the case of an arbitrary variation of the temperature.

A nonlinear isoconversional method[9] avoids approximations of the temperature integral. Using the aforementioned basic assumption, one can write, for a given conversion and a set of experiments performed under different heating rates β_i ($i = 1, \ldots, n$):

$$(A_\alpha/\beta_1)I(E_\alpha, T_{\alpha,1}) = (A_\alpha/\beta_2)I(E_\alpha, T_{\alpha,2})$$
$$= \cdots = (A_\alpha/\beta_n)I(E_\alpha, T_{\alpha,n})$$
$$(6)$$

After canceling A_α, eq. (6) can be represented as a condition of minimum value:

$$\sum_{i \neq j}^n \sum^n \left[I(E_\alpha, T_{\alpha,i})\beta_j \right] \Big/ \left[I(E_\alpha, T_{\alpha,j})\beta_i \right] = \min \quad (7)$$

Substituting experimental values of T_α and β into eq. (7) and varying E_α to reach the minimum gives the value of the activation energy at a given conversion.[9]

Although eqs. (6) and (7) underlying the nonlinear isoconversional method only hold for a linear heating program, they can be adapted to an arbitrary variation of the temperature. Let us introduce a function:

$$J[E, T(t)] = \int_0^t \exp[-E/RT(t)]\,dt$$

and assume that the reaction model, $g(\alpha)$, is independent of the variation of the temperature. Then we can write for a given conversion and a set of experiments performed under n different pre-

scribed heating programs:

$$A_\alpha J[E_\alpha, T_1(t_\alpha)] = A_\alpha J[E_\alpha, T_2(t_\alpha)]$$
$$= \cdots = A_\alpha J[E_\alpha, T_n(t_\alpha)] \quad (8)$$

where $T_i(t)$ $(i = 1, \ldots, n)$ is meant to be the actual variation of temperature. It is implicitly assumed that the use of different prescribed programs gives rise to different temporal variations of the actual temperature inside the sample. After canceling A_α, eq. (8) is reduced to the condition of a minimum (9):

$$\Phi(E_\alpha) = \sum_{i \neq j}^{n} \sum^{n} J[E_\alpha, {}_i(t_\alpha)] \Big/ J[E_\alpha, T_j(t_\alpha)] = \min$$
$$(9)$$

Substituting the time, t_α, for which a given conversion has been reached and the actual temperature at that moment, into eq. (9) and varying E_α until the minimum is attained gives an estimate of the activation energy. This procedure is to be repeated for different conversions to obtain a dependence of E_α on α.

Eq. (9) is the basic equation of the integral isoconversional method applicable to an arbitrary variation of temperature. It imposes no restrictions on the form of $T(t)$ and may be applied to the ''time−temperature−yield'' data ascertained from any experimental technique, provided that the actual variation of the temperature inside the reaction system can be experimentally measured as a function of time. A numerical algorithm to solve eq. (9) is now given in full detail.

Computational Aspects of the Method

COMPUTATION OF INTEGRALS IN EQ. (9)

To compute the integrals in eq. (9) one has to find the value of J_0:

$$J_0 = J[E, T(t_0)] = \int_0^{t_0} \exp[-E/RT(t)]\, dt \quad (10)$$

where t_0 is the time corresponding to the first experimental measurement. In practice, t_0 is usually taken equal to 0, which is equivalent to $J_0 = 0$ and means that no reaction occurred before this moment. Nevertheless, theoretically, a reaction occurs at any T exceeding absolute zero. Thus, t_0 means the time required for the temperature of a reaction system to rise from absolute zero to the

initial (ambient) temperature, T_0, under the current heating program. If $T(t)$ is given by an analytical function, the integral is defined over the whole interval of t, and t_0 can easily be found from the condition $T(t_0) = T_0$. For an arbitrary variation of the temperature, the integral $J[E, T(t)]$ is defined only over the interval of experimental measurements. This makes a direct evaluation of J_0 impossible. To estimate J_0 we have to resort to extrapolation.

In the case of an arbitrary variation of temperature, the following procedure can be applied to estimate J_0. Experimental values of T versus t are approximated in the neighborhood of T_0 by a polynomial, or another nonlinear function, as $t = f(T)$ from which t_0 is estimated as $-[f(T)]_{T=0}$. The value of t_0 is added to the experimental values of t. Then these corrected values are used to approximate $T(t)$ by a nonlinear function in the neighborhood of T_0. The approximated $T(t)$ is then extrapolated to the time region of $0 - t_0$ to evaluate J_0.

For the majority of actual experimental conditions, however, $T(t)$ at $t < t_0$ can be reasonably approximated by a linear function in the neighborhood of T_0. Under this assumption, the integral over time in eq. (10) can be replaced with the integral over temperature as follows:

$$J_0 = (\beta^*)^{-1} I(E, T_0) \quad (11)$$

where β^* is the quasilinear heating rate which is defined as the slope of T against t taken from the first several points of the experimental dependence of T on t. The advantage of the approximation of a quasilinear heating rate is that the temperature integral, $I(E, T_0)$, can be replaced by the very simple and accurate approximation of Senum and Yang[10]:

$$J_0 \approx (\beta^*)^{-1}(E/R)\exp(-x)/x$$
$$\times (x^2 + 10x + 18)/(x^3 + 12x^2 + 36x + 24)$$
$$(12)$$

(where $x = E/RT_0$) whose deviations do not exceed $2 \cdot 10^{-3}\%$ at $x > 10$.

Therefore, in the approximation of a quasilinear heating rate the integrals, $J[E, T(t)]$, in eq. (9) can be represented as:

$$J[E, T(t)] = J_0 + \int_{t_0}^{t} \exp[-E/RT(t)]\, dt \quad (13)$$

where J_0 is computed by eq. (12). To compute the integral over the time in eq. (13), we used Simp-

son's rule.[11] The step of integration was taken so that, overall, 5000 points fell on each α versus t curve. The values of α and T corresponding to equidistant values of t have been found by a nonlinear interpolation[11]:

$$f(x_0) = af_{l-1} + bf_l + cf_{l+1} \qquad (14)$$

$$a = (x_0 - x_l)$$
$$\times (x_0 - x_{l+1})/[(x_{l-1} - x_l)(x_{l-1} - x_{l+1})]$$
$$b = (x_0 - x_{l-1})$$
$$\times (x_0 - x_{l+1})/[(x_l - x_{l-1})(x_l - x_{l+1})]$$
$$c = (x_0 - x_{l-1})$$
$$\times (x_0 - x_l)/[(x_{l+1} - x_{l-1})(x_{l+1} - x_l)]$$

where $x_{l-1} < x_l < x_{l+1}$ are three successive points taken as $x_{l-1} < x_0 < x_{l+1}$.

COMPUTATION OF E_α BY EQ. (9)

The use of eq. (9) requires determination of the values of the time and temperature corresponding to given conversions. For this purpose, the entire interval of conversions, $[0, 1]$, has been represented by a set of equidistant values of α. Then the necessary values of t_α and T_α have been found by respective nonlinear interpolations, $T = f(\alpha)$ and $t = f(\alpha)$. The latter have been built up in the form of eq. (14) using actual values t, T, and α.

An initial estimate, E_0, for E_α is found under the assumption that $\Phi(E_\alpha)$ can be approximated by a quadratic parabola:

$$\Phi(E_\alpha) = aE_\alpha^2 + bE_\alpha + c \qquad (15)$$

Choosing the interval of variation of E_α as E_1 and E_2 (we used the values of $E_1 = 4 \cdot 10^3$ and $E_2 = 4 \cdot 10^6$ J mol^{-1}) and computing $\Phi(E_\alpha)$ at E_1, E_2, and $E_3 = (E_1 + E_2)/2$ one can determine the coefficients of eq. (15). Then E_0 is estimated as an abscissa related to the minimum of a quadratic parabola:

$$E_0 = -b/2a$$

Our computations on model data have shown that E_0 is a very close estimate for the actual value of E_α. The deviations of E_0 from the final value of the activation energy found by the numerical algorithm described below were within 5% of the final value. The value of E_0 is used to set new limits on the interval of E_α variation. The limits are taken as $E_1 = 0.95$, E_0 and $E_2 = 1.05E_0$. A search for the minimum of eq. (9) starts if the condition of $\Phi(E_1)$ $> \Phi(E_1 + \delta)$ (where $\delta > 0$) is satisfied. Otherwise, E_1 is iteratively reduced by a factor of 0.95 until the condition of $\Phi(0.95E_1) > \Phi(E_1)$ is reached. A minimum for eq. (9) is found by varying E_α with a step $\delta = (E_2 - E_1)/5$, starting from E_1 and until $\Phi(E_\alpha + \delta) > \Phi(E_\alpha)$. Then the values of $E_\alpha - \delta$ and $E_\alpha + \delta$ are, respectively, assigned to E_1 and E_2 and a new value of δ is determined. The search is repeated while $\delta > 1$ kJ mol^{-1}. Once the latter condition has been fulfilled, the value of E_α is considered to be the sought value of the activation energy at a given conversion. To compute the entire dependence of E_α on α, the above procedure should be repeated as many times as the number of the equidistant values, α, chosen to represent this dependence.

Simulated data have been used to test the integral isoconversional method eq. (9) subject to the approximation of a quasilinear heating rate and to the above algorithm to compute E_α. Data have been simulated for a set of the reaction models (Table I) with $E = 125.4$ kJ mol^{-1} and $A = 10^{15}$ min^{-1} under the conditions of linear and hyperbolic heating.

Linear heating data have been simulated at heating rates, β_i, of 8, 12, and 16 K min^{-1}. The dependence of α on T has been found by integrating eq. (3) in the approximation of Senum and Yang.[10] The conversions related to a given reaction model, $g_k(\alpha)$ (Table I), and to given temperatures have been found through the inverse transformation:

$$\alpha = G_k[(A/\beta_i)I(E, T)] \qquad (16)$$

here G_k is a function inverse to $g_k(\alpha)$. The corresponding time values have been calculated as follows:

$$t = (T - T_0)/\beta_i$$

where T_0 was taken to be 293 K.

The hyperbolic heating data have been simulated for the following heating program:

$$T(t) = (T_0^{-1} - \mu_i t)^{-1} \qquad (17)$$

with the μ_i values of $6 \cdot 10^{-5}$, $9 \cdot 10^{-5}$, and $1.2 \cdot 10^{-4}$ min^{-1} K^{-1}. The values were chosen so that the corresponding quasilinear heating rates, β^*, were close to the values of 8, 12, and 16 K min^{-1}, respectively. The heating program eq. (17) allows for an exact solution[3] of the temperature integral giving rise to:

$$g(\alpha) = (AR/\mu_i E)\exp(-E/RT) \qquad (18)$$

The inverse transformation similar to eq. (16):

$$\alpha = G_k[(AR/E\mu_i)\exp(-E/RT)]$$

has been used to obtain α on T dependencies for different reaction models, $g_k(\alpha)$, and the values of μ_i as follows:

$$t = (T_0^{-1} - T^{-1})/\mu_i$$

where T_0 was taken to be 293 K.

The accuracy of the algorithm has been estimated by the deviation of E_α evaluated by eq. (9) from the value of E used to simulate the data. The deviations have been averaged over the whole set of conversions:

$$\Omega = (1/m) \sum_{l=1}^{m} |E_{\alpha,l} - E|/E \qquad (19)$$

where $l = 1 \ldots m$ is the number of equidistant values of α. The values of Ω are given in Table II for both linear and hyperbolic heating programs. It is seen that the accuracy of evaluating E_α varies with the model, amounting to an average of about 1.1–1.2%. Note that even an extreme deviation of 2.9% is well within the generally accepted 5% error for the activation energy.

Another important result of the above comparison is that the values of the deviation in the activation energy for the same reaction model do

TABLE II.
Deviations (Ω) in E_α [Computed by Eq. (9)] for Processes Simulated by Different $g(\alpha)$ (Table I) for Linear and Hyperbolic Heating Program.[a]

N	Linear program		Hyperbolic program	
	Ω (%)	τ (sec)	Ω (%)	τ (sec)
1	2.3	13.6	2.1	12.9
2	1.0	15.8	2.3	12.6
3	0.4	13.3	0.3	13.6
4	0.7	12.0	1.0	13.9
5	0.9	12.6	0.3	11.4
6	0.7	10.1	0.3	10.7
7	2.9	11.7	2.5	10.1
8	0.7	10.7	2.6	11.4
9	0.7	10.1	1.0	11.7
10	1.0	10.4	1.0	12.0
11	0.6	11.7	0.7	12.6
12	0.8	12.0	0.6	12.3
Average	1.1	12.0	1.2	12.1

[a] τ is the computation time; that is, the time elapsed to find a single E_α value using an Intel 75-MHz Pentium processor.

not show any obvious increase when changing from the linear to hyperbolic heating program. This certainly lends support to the validity of the approximation of the quasilinear heating rate to estimate J_0.

Model Example

As previously mentioned, nonlinear heating programs are not widely used to study the mechanism and kinetics of thermally stimulated reactions. The most commonly encountered heating programs are linear programs. A reaction system exposed to such heating experiences a linear variation of temperature with possible nonlinear deviations caused by the thermal effects of the process. Therefore, a process proceeding at a linear variation of temperature complicated by nonlinear deviations is believed to be a very realistic model example.

Assume that the nonlinear deviation in temperature, which is proportional to $\Theta(T)$, follows the Gaussian function:

$$\Theta(T) = (a/w)(\pi/2)^{-1/2}$$
$$\times \exp\left\{-2[(T - T_m)/w^2]^{1/2}\right\} \quad (20)$$

where T_m is the temperature corresponding to a maximum deviation of the actual temperature from a prescribed program, w is approximately the width of the peak at half-height, and a is the total area of the peak. Eq. 20 with parameters $a = 12.6$ and $w = 10$ gives a peak with the amplitude, $\Theta(T_m) \approx 1$ and width, $T_f - T_i \approx 30$ K [the initial T_i and final T_f temperatures are defined as $\Theta(T_i)$ and $\Theta(T_f) \approx 0.1$ K]. Then the following equation:

$$T_i(t) = T_o + \beta_i t + \delta T \Theta(T_o + \beta_i t) \quad (21)$$

can be used to simulate the required temperature variations with a given maximum deviation, δT.

Mampel's reaction model[12] (N6 in Table I) with Arrhenius parameters of $E = 125.4$ kJ mol^{-1} and $A = 10^{15}$ min^{-1} has been used to simulate data. The temperature has been varied, by eq. (21), at five δT values of 0, ± 5, and ± 10 K, which are typical of solid-state transformations.[5] For each given value of δT, the data have been simulated at three heating rates, $\beta_i = 8, 12, 16$ K min^{-1}. The values of t, T, and α have been found by numeri-

cal integration:

$$\alpha = 1 - \exp\{-J[E, T_i(t)]\} \qquad (22)$$

using Simpson's rule. The values of T_m in eq. (20) were conventionally taken equal to the temperatures at which $d\alpha/dT$ is maximum under conditions of a linear heating. For the reaction and the heating rates being considered, this temperature corresponds to an approximately constant value of $\alpha \approx 0.61$. The results of simulations are shown in Figures 1 and 2. Notice that the distortion of a sigmoid shape similar to that shown in Figure 2 is usually attributed to complex kinetics. However, one should keep in mind that such distortions may also be due to the temperature deviations induced by the thermal effect of the process.

As was previously mentioned, if a computational method does not account for the actual variation of temperature, its deviations from the prescribed program result in erroneous values of the activation energy. The results of such computations were examined on the above-simulated data by the nonlinear isoconversional method[9] based on eq. (7), which holds only for a linear heating program. The data have been processed on the assumption that the actual temperature strictly obeys a linear program; that is, as though δT in eq. (21) was zero. The results are presented in Figure 3.

FIGURE 2. Simulated conversion–temperature data at $\beta = 12\ \mathrm{K\,min^{-1}}$ and at different values of δT (see notations to Fig. 1).

Because the data have been simulated for a single-step reaction, the computed values of the activation energy must be constant throughout the entire interval of conversions. The results, however, clearly demonstrate a systematic dependence
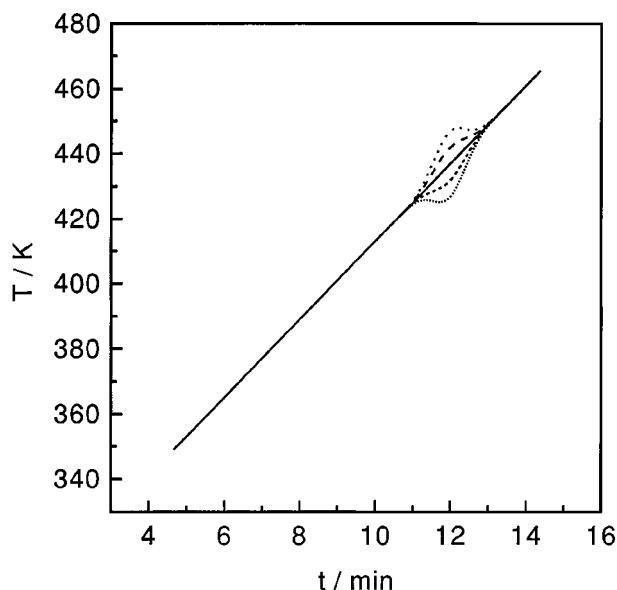

FIGURE 1. Variation of the temperature [eq. (21)] used to simulate data (solid: $\delta T = 0$; dash: $\delta T = +5$; short dash: $\delta T = -5$; dot: $\delta T = +10$; short dot: $\delta T = -10$).
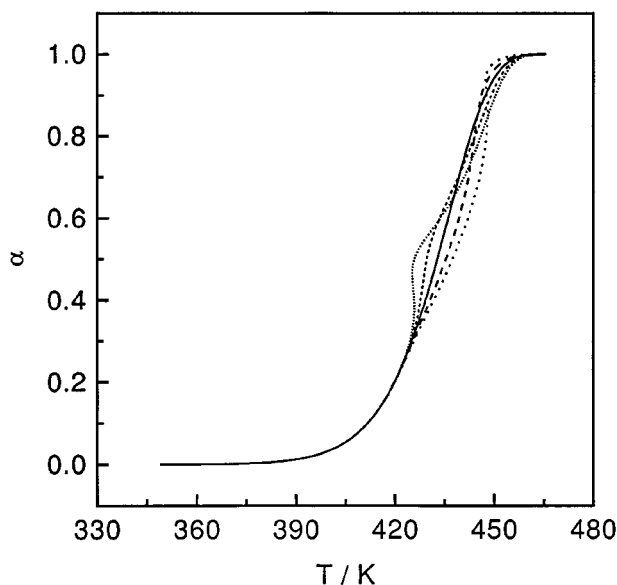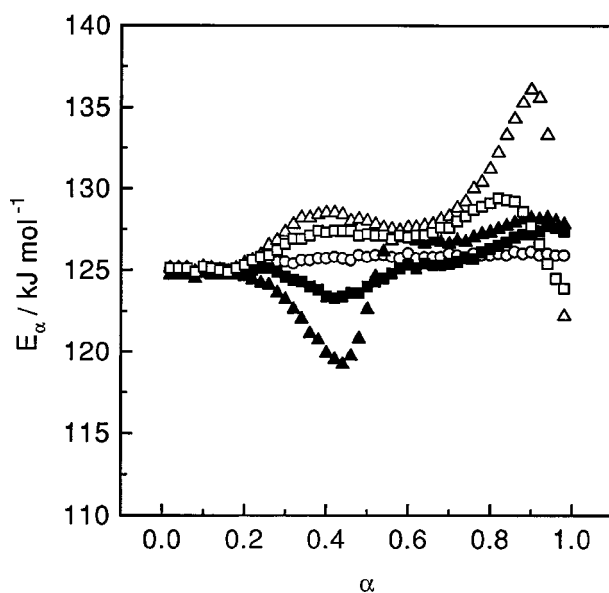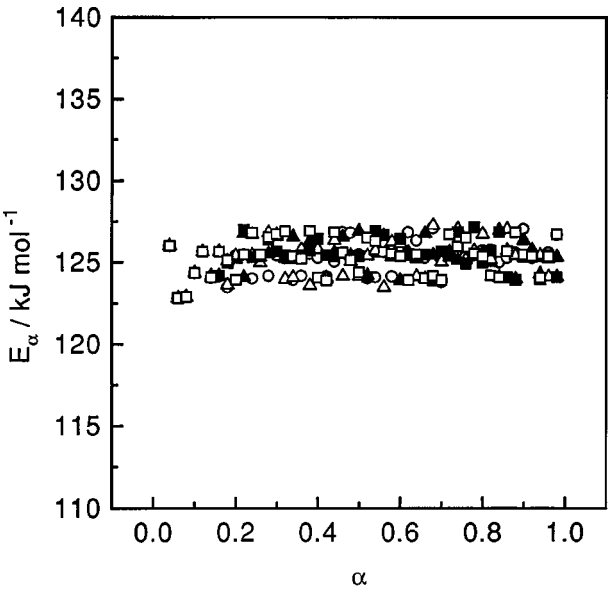

FIGURE 3. Values of the activation energy [computed by eq. (7)] for the simulated process at variations of temperature [by eq. (21)] with different values of δT (circles: $\delta T = 0$; open squares: $\delta T = +5$; solid squares: $\delta T = -5$; open triangles $\delta T = +10$; solid triangles $\delta T = -10$).

of E_α on α. The occurrence of such a dependence could easily be interpreted in terms of complex reaction mechanisms.[6] However, the present example shows that, before interpreting the dependence of E_α on α, the actual variation of the temperature should be tested for consistency with a prescribed program. An adequate mechanistic interpretation of the dependence of E_α on α is allowable only if a prescribed program has been obeyed. Otherwise, the interpretation is problematic because both factors, temperature deviations and complex kinetics, manifest themselves as a dependence of E_α on α. This means that temperature deviations may disguise the potential complexity of a process.

Let us now consider the results of data processing by the isoconversional method which holds for an arbitrary variation of temperature [eq. (9)]. The dependencies computed are presented in Figure 4. It is immediately apparent that the results of computations are entirely independent of the δT value. All values of E_α are clustered around 125.4 kJ mol^{-1} which was used to simulate the data. Extreme deviations do not exceed 2% of this value, amounting on average to about 0.7% (Table III). The fact that the value of δT does not influence the deviations in the activation energy allows us to attribute them to the computational features of the

TABLE III.
Deviations (Ω) in E_α [Computed by Eq. (9)] for the Simulated Process Exposed to a Nonlinear Heating Program [Eq. (21)].[a]

δT (K)	Ω (%)	τ (sec)
0	0.6	10.9
+5	0.7	10.5
−5	0.7	11.3
+10	0.7	10.7
−10	0.6	11.3
Average	0.7	10.9

[a] τ is the computation time; that is, the time elapsed to find a single E_α value using an Intel 75-MHz Pentium processor.

method and most likely to Simpson's rule used for numerical integration.

The computations of a single E_α value take 10−16 seconds (Tables II and III). Therefore, a representative dependence of E_α on α, similar to those shown in Figure 4, can be obtained in 8−13 minutes.

Tolerance of the Method for Experimental Noise in the Temperature

Tolerance of the method has been tested using the above model example. It has been assumed that the temperature measurements, $T_i(t)'$, contain noise which is subject to the normal distribution:

$$T_i(t)' = T_i(t) + cN_i \qquad (23)$$

where $T_i(t)$ is the temperature found by eq. (21); N_i is a random value obeying the standard normal distribution,[11] $N(0, 1)$; and c is the scaling factor having dimensions of the temperature.

To simulate the values of N_i, the built-in function `random` (Borland Turbo Pascal 6.0) has been used. This function generates pseudorandom numbers, R_i, which have the uniform (rectangular) distribution, $R(\mu, \sigma^2)$. By the central limit theorem,[11] these numbers can be used to generate values, N, obeying the standard normal distribution as follows:

$$N = \left[(1/n) \sum_{i=1}^{n} R_i - \mu \right] \Big/ (\sigma^2/n)^{1/2} \qquad (24)$$

FIGURE 4. Values of activation energy [computed by eq. (9)] for the simulated process at variations of temperature [by eq. (21)] with different values of δT (see notations to Fig. 3).

where μ is the mean and σ^2 is the variance of the uniform distribution. If the function `random` is set to yield R_i within the interval of $[0, 1]$, then $\mu = 1/2$ and $\sigma^2 = 1/12$.[11] This enables eq. (24) to be reduced to:

$$N = \left(\sum_{i=1}^{n} R_i - n/2 \right) \bigg/ (n/12)^{1/2} \qquad (25)$$

The approximation [eq. (25)] rapidly increases in accuracy with n. It has been mentioned,[13] that for practical purposes, it is sufficient to take $n = 12$. In our simulations, the value of n was set to be 100.

To simulate experimental noise of different levels, we used the following values of c: 0.1, 0.2, 0.5, and 1.0 K. According to the normal distribution we can expect, with a 95% probability, that the maximum value of cN_i in eq. (23) does not exceed $2c$. In other words, no more than 1 in every 20 temperature measurements is likely to have a random error exceeding $2c$.

The results of the computations by eq. (9) for the data with different levels of experimental noise are given in Table IV. Introduction of noise causes no significant shifts in the average value of E_α. However, the value of average deviation, Ω, found by eq. (19), increases with the level of noise (Fig. 5). The fact that Ω tends to increase linearly with c, suggests that the method has the same degree of tolerance at different levels of noise in the temperature. Figure 5 also shows that E_α can be evaluated with at least 5% accuracy, if random errors in the temperature exceeding 1 K ($c = 0.5$ K) do not occur more often than 1 in every 20 measurements. This condition seems to be achievable in usual experiments. Hence, the method can be recommended for practical use.

TABLE IV.
Effect of Experimental Noise of Different Levels [Eq. (23)] on Average Values of E_α Computed by Eq. (9) for the Simulated Process Exposed to a Nonlinear Heating Program [Eq. (21)].

δT (K)	E (kJ mol^{-1})				
	0*	0.1*	0.2*	0.5*	1.0*
0	125.2	124.9	124.6	125.5	128.0
+5	125.3	125.1	126.3	125.2	126.6
−5	125.3	124.9	125.0	125.5	126.0
−10	125.3	125.2	123.9	125.2	125.9
+10	125.3	125.5	124.6	129.9	129.0

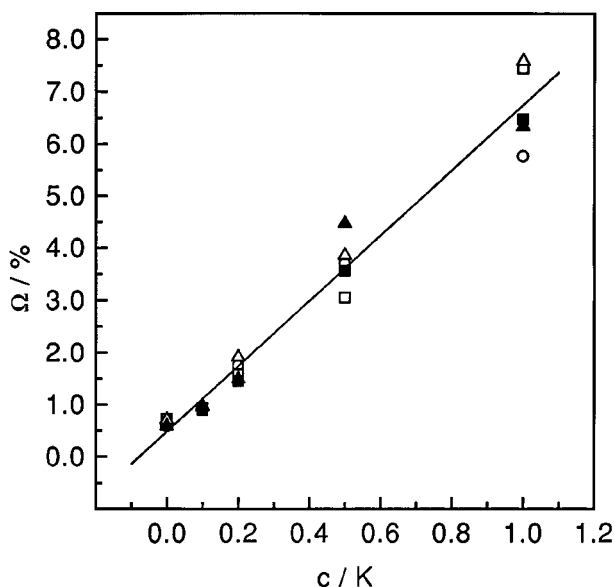*Level of experimental noise, c(K).

FIGURE 5. Deviations in E_α, Ω, computed for different levels of experimental noise, c (see notations to Fig. 3).

Conclusions

The suggested isoconversional method has been tested and found to be adequate for kinetic computations when a reaction system undergoes arbitrary variation of the temperature. The foregoing tests have demonstrated that the activation energies estimated by this method are characterized by only minor inaccuracy which lies within a commonly acceptable 5% level. Tolerance of this method for noise in the temperature shows its potential for practical applications. This method is expected to be of profound interest in studying the reaction kinetics in systems which cannot, in principle, obey a prescribed heating program because of significant thermal effects. The use of this method can help to avoid the necessity of development of intricate experiments designed to lessen temperature deviations. Although the method has been developed bearing in mind the reactions of solids, it is believed that it can be applied to other heterogeneous and homogeneous reactions whose kinetics are affected by arbitrary variations of temperature due to thermal effects.

Acknowledgment

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