

# Linear and Nonlinear Procedures in Isoconversional Computations of the Activation Energy of Nonisothermal Reactions in Solids

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An integral isoconversional method provides a linear procedure to estimate the activation energy ( $E_\alpha$ ) at a given conversion ( $\alpha$ ) but only when an oversimplified approximation of the temperature integral ( $p(x)$ , where  $x = E/RT$ ,  $R$  is the gas constant and  $T$  is the temperature) is used. Although the relative error in  $E_\alpha$  is several times less than the relative error in  $p(x)$  it happens to be substantial at  $x < 13$ . In the present study a nonlinear procedure to estimate  $E_\alpha$  has been developed. It shows very low relative errors in  $E_\alpha$  which are practically independent of  $x$ . The computations have been performed for model reactions as well as for the thermal decomposition of  $\text{Cu}_4\text{OCl}_6(\text{triphenylphosphine oxide})_4$ .

## INTRODUCTION

The kinetics of reactions in solids are usually described<sup>1</sup> by eq 1

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

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

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

(where  $A$  is the pre-exponential factor,  $E$  is the activation energy, and  $R$  is the gas constant). Equation 2 as well as numerous approximations of its integral form (3)

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

(where

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

is the integral form of the reaction model (Table 1)) underlies most of the methods of kinetic processing. Those which are used most frequently<sup>1</sup> employ data obtained under one heating rate alone. These methods use fitting alternative reaction models to experimental data to evaluate Arrhenius parameters. The latter are, therefore, inevitably tied up with a reaction model. The problem here is that usually quite different reaction models fit the data equally well (from the statistical point of view), whereas the numerical values of the corresponding Arrhenius parameters crucially differ.<sup>2</sup>

The ambiguity of the kinetic triplet ( $E$ ,  $A$ ,  $f(\alpha)$ , or  $g(\alpha)$ ) creates problems of its practical use for predicting the behavior of a substance over the range of experimental temperatures. Reliable predictions play an important role especially when common techniques such as thermogravimetry or differential scanning calorimetry are not applicable

**Table 1.** Set of Alternate Reaction Models Applied To Describe the Thermal Transformations in Solids

$N$	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	$1/2\alpha^{-1}$	$\alpha^2$
6	first-order (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	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$

because of either very slow or very fast reaction rate. The thermal behavior of solids under the storage (ambient temperatures) or combustion (elevated temperatures) provides two everyday examples. However, the ambiguity of the kinetic triplet entails such imprecise predictions that they have no practical value.<sup>3</sup>

The ambiguity can be overcome when using multiheating rate methods such as isoconversional methods of Friedman,<sup>4</sup> Ozawa,<sup>5</sup> and Flynn and Wall.<sup>6</sup> These methods allow one to obtain at each given conversion the activation energy,  $E_\alpha$ , which is independent of the reaction model or, in other words, single-valued. The pre-exponential factor can also be evaluated<sup>7</sup> independently of the reaction model. Once the values of the activation energy and the pre-exponential factor have been determined, the reaction model can be reconstructed in the tabular form to which an explicit form of the reaction model can be fitted.<sup>8</sup> The isoconversional methods can be applied to multistep reactions. In such a case these methods reveal a dependence of the activation energy on conversion. The shape of this dependence is indicative of the reaction mechanism.<sup>9</sup>

It is noteworthy that the sole dependence of the activation energy on conversion is sufficient to reliably predict the behavior of a substance.<sup>3,10</sup> The accuracy of such predictions obviously depends on the accuracy of computing the activation energy. This brings to the fore the problem of minimizing errors in computing the activation energy. One of the sources of these errors is oversimplified approxima-

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tions of the temperature integral in (3). Such approximations are intentionally used to derive the simplest (i.e., linear) final plots yielding the activation energy. Approximations undeniably induce an error in the value of the activation energy. However, the question is how does an approximation of the temperature integral influence the error in evaluating the activation energy? To find an answer for this question a nonlinear procedure for computing the activation energy by the isoconversional method has been developed. The intention of this paper is to report an algorithm of this procedure and to compare the values of the activation energy computed by the common linear and suggested nonlinear procedures.

#### LINEAR PROCEDURE IN THE ISOCONVERSIONAL METHOD

As it was mentioned in above, most of the methods of kinetic computations are based on the integral eq 3. The integrated form of (3) is usually represented<sup>1</sup> as

$$g(\alpha) = (AE/\beta R) p(x)$$

where  $x = E/RT$  and  $p(x)$  is an approximation of the temperature integral. The Doyle's approximation<sup>11</sup>

$$\ln p(x) = -5.33 - 1.05x$$

leads to linear equations of Ozawa<sup>5</sup> and Flynn and Wall.<sup>6</sup> These methods give  $E_\alpha$  from the plot  $\ln \beta_i$  vs  $T_{\alpha,i}^{-1}$ . As the approximation is not exact at  $x < 20$  both methods require further corrections<sup>12</sup> of the  $E_\alpha$  value.

The generalized eq 4

$$p(x) = \exp(-x)/x^2 [(1 - 2/x)/(1 - m/x^2)] \quad (4)$$

combines<sup>13</sup> several previously suggested approximations ( $m$  is a parameter specifying a given approximation). Equation 4 gives rise to (5)

$$\ln(\beta_i/T_{\alpha,i}^2) = \ln\{(A_\alpha R/E_\alpha g(\alpha)) [(1 - 2/x)/(1 - m/x^2)]\} - E_\alpha/RT_{\alpha,i} \quad (5)$$

which is practically linear with respect to  $T_{\alpha,i}^{-1}$  at  $x > 10$  and thus allows  $E_\alpha$  to be found from the slope of the plot of  $\ln(\beta_i/T_{\alpha,i}^2)$  vs  $T_{\alpha,i}^{-1}$ . Generally, the use of this plot means that the part  $(1 - 2/x)/(1 - m/x^2)$  of the approximation 4 is neglected, and an oversimplified approximation 6

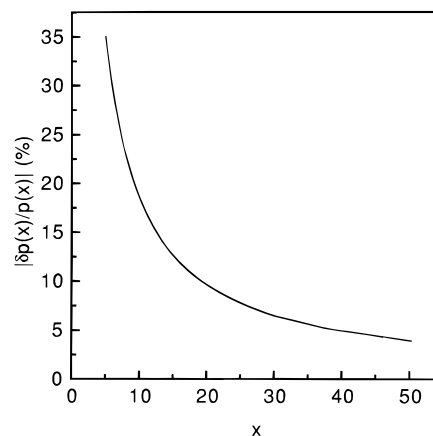
$$p(x) = \exp(-x)/x^2 \quad (6)$$

is actually used. Figure 1 shows a relative error caused by the above approximation in the temperature integral at different  $x$  values.

Therefore, only oversimplified approximations of the temperature integral lead to linear equations to evaluate the activation energy. In this paper the dependence of  $\ln(\beta_i/T_{\alpha,i}^2)$  vs  $T_{\alpha,i}^{-1}$  based on approximation 6 has been used to evaluate  $E_\alpha$ . In further discussion this type of calculations will be referred to as *the linear procedure*. An alternative nonlinear procedure is proposed in the following section.

#### NONLINEAR PROCEDURE IN THE ISOCONVERSIONAL METHOD

Let us introduce a function 7



**Figure 1.** Relative error in the approximation of the temperature integral by eq 6.

$$I(E,T) = \int_0^T \exp(-E/RT) dT \quad (7)$$

With regard to (7) eq 3 takes the form of (8)

$$g(\alpha) = (A/\beta)I(E,T) \quad (8)$$

Using a general assumption<sup>4-6</sup> that the reaction model is independent of the heating rate, eq 8 can be written for a given conversion and a set of experiments performed under different heating rates  $\beta_i$  ( $i = 1, \dots, n$ ) as (9)

$$(A_\alpha/\beta_1)I(E_\alpha, T_{\alpha,1}) = (A_\alpha/\beta_2)I(E_\alpha, T_{\alpha,2}) = \dots = (A_\alpha/\beta_n)I(E_\alpha, T_{\alpha,n}) \quad (9)$$

It follows from the strict fulfillment of (9) that

$$\sum_{i \neq j}^n \sum_j^n [I(E_\alpha, T_{\alpha,i})\beta_j]/[I(E_\alpha, T_{\alpha,j})\beta_i] = n(n-1) \quad (10)$$

where  $j = 1, \dots, n$ . Since the  $T_\alpha$  values are measured with some experimental error, (9) can only be satisfied as an approximate equality. Consequently, (10) may be satisfied as a condition of minimum value

$$|n(n-1) - \sum_{i \neq j}^n \sum_j^n \{[I(E_\alpha, T_{\alpha,i})\beta_j]/[I(E_\alpha, T_{\alpha,j})\beta_i]\}| = \min \quad (11)$$

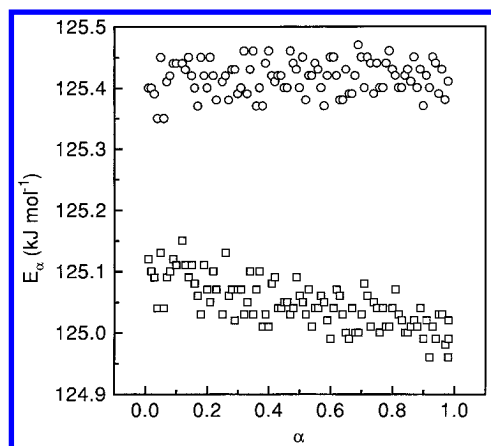
The nonlinear eq 11 may be easily used to obtain  $E_\alpha$ . Substituting experimental values of  $T_\alpha$  and  $\beta$  into (11) and varying  $E_\alpha$  to reach the minimum gives the value of the activation energy at a given conversion. The values of  $I(E,T)$  can be found by numerical integration which is, however, a very time consuming procedure in the case of the temperature integral. For instance, the computation of one  $I(E,T)$  value by the trapezoidal rule with the step  $10^{-2}$  K requires about  $10^4$  more time than when using the Senum-Yang approximation<sup>14</sup>

$$p(x) = \exp(-x)/x(x^2 + 10x + 18)/(x^3 + 12x^2 + 36x + 24) \quad (12)$$

The use of the latter seems quite reasonable as this approximation even at  $x = 5$  gives only 0.02% deviation from the exact value of the temperature integral.<sup>14</sup> As can

**Table 2.** Arrhenius Parameters and Ranges of Variation of  $x$  Values

$N$	$E$ (kJ mol <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$x$
1	20.9	10 <sup>2</sup>	6.5–7.0
2	41.8	10 <sup>4</sup>	10.9–12.8
3	83.6	10 <sup>6</sup>	15.5–19.6
4	125.4	10 <sup>10</sup>	24.3–27.9
5	167.2	10 <sup>18</sup>	42.1–46.0

**Figure 2.** Comparative values of the activation energy computed for a first order model process with  $E = 125.4$  kJ mol<sup>-1</sup> and  $A = 10^{10}$  min<sup>-1</sup>. Henceforth open circles and squares relate to the nonlinear and linear procedures, respectively.

be seen from the results of this work such deviations do not practically affect the values of the activation energy.

Numerical solution of (11) in the approximation (12) will be used to evaluate  $E_\alpha$ . In further discussion this type of calculations will be referred as *the nonlinear procedure*.

#### DATA MODELING

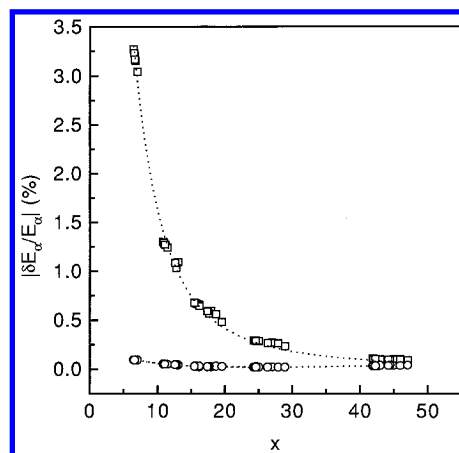
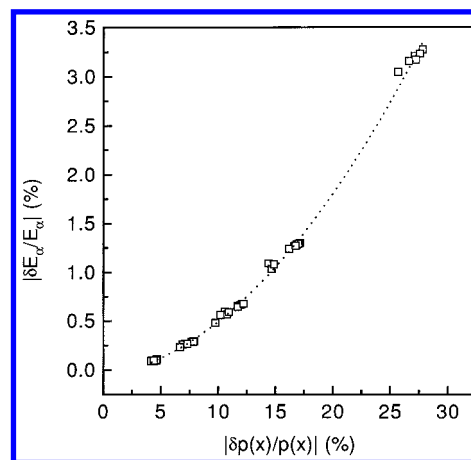
Data have been simulated at the heating rates of  $\beta = 8, 12, 16, 20$  K min<sup>-1</sup>. The  $T_\alpha$  values required for isoconversional method were found as a numerical solution of eq 13

$$\alpha - G[AI(E,T)/\beta] = 0 \quad (13)$$

(where  $G$  is a function inverse to  $g(\alpha)$ ) for a set of the  $\alpha$  values of 0.01–0.99 (step 0.01) by varying  $T$  so that the left hand side of (13) did not exceed  $10^{-5}$ . The integral over temperature in (13) was replaced by the Senum–Yang approximation (12). The data were modeled using each of the 12 reaction models from Table 1. The Arrhenius parameters used to model data are given in Table 2. Since not only Arrhenius parameters but also the reaction model and the heating rate define the temperature region of a reaction, the  $x$  value happens to be variable at constant  $A$  and  $E$ . Table 2 shows actual regions of  $x$  variation.

#### RESULTS AND DISCUSSION

Applying the linear and nonlinear procedures to model data, the values of  $E_\alpha$  for all model reactions were found. Figure 2 shows some results of these computations for a first-order reaction with  $E = 125.4$  kJ mol<sup>-1</sup>. It is seen that the  $E_\alpha$  values computed by the nonlinear procedure are clustered around the exact value of the activation energy. The values found by the linear procedure not only are displaced from the exact value but also have a trend to systematically depart with increasing conversion. Since the latter is accompanied

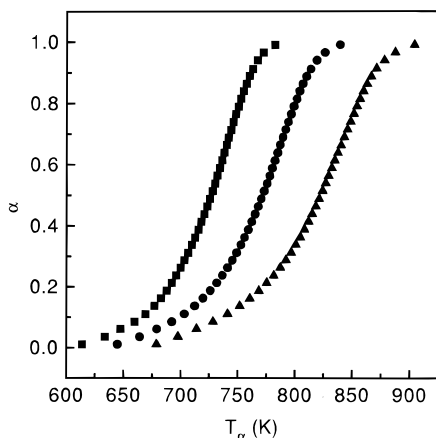
**Figure 3.** Relative error in the activation energy computed by the linear and nonlinear procedures.**Figure 4.** Correlation between the relative error in the activation energy computed by the linear procedure and the relative error in the approximation of the temperature integral by eq 6.

by increasing the temperature the observed trend seems to have resulted from decreasing both the value of  $x$  and correspondingly exactness of the temperature integral approximation.

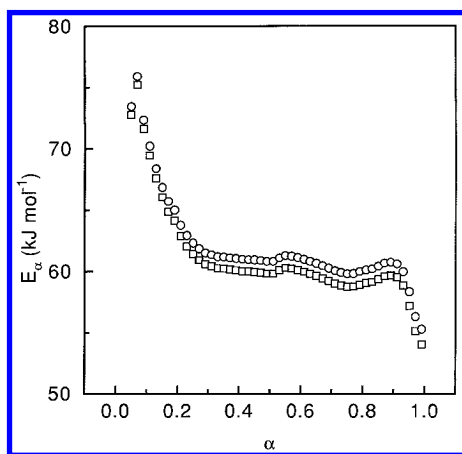
Figure 3 provides a comparison of relative deviations of the computed activation energy from the exact value as a function of the  $x$  value. The nonlinear procedure reveals extremely low errors ( $<0.1\%$ ) in the activation energy. Another important fact is that this procedure virtually shows no dependence of  $|\delta E_\alpha/E_\alpha|$  on  $x$ . This evidently suggests that the use of the Senum–Yang approximation in the nonlinear procedure instead of an exact numerical solution is harmless even at small  $x$  values.

The linear procedure demonstrates increasing deviation with decreasing  $x$  (Figure 3). Since 5% error in the activation energy used to be considered as reasonable, we can possibly accept an error less than 1% that appears with the introduction of the approximation of the temperature integral. With regard to our data (Figure 3) this means that generally the linear procedure may be used at  $x > 13$ .

Let us elucidate how the error in the temperature integral caused by the approximation 6 affects the error in the activation energy evaluated by the linear procedure. Figure 4 presents a dependence of  $|\delta E_\alpha/E_\alpha|$  vs  $|\delta p(x)/p(x)|$ . This dependence has been found by coupling the values of  $|\delta p(x)/p(x)|$  (Figure 1) and  $|\delta E_\alpha/E_\alpha|$  (Figure 3) related to the same  $x$  values. It follows from this dependence that the effect of



**Figure 5.** The  $\alpha$  vs  $T_\alpha$  data for the thermal decomposition of  $\text{Cu}_4\text{-OC16}(\text{triphenylphosphine oxide})_4$  at different heating rates (squares,  $5 \text{ K min}^{-1}$ ; circles,  $10 \text{ K min}^{-1}$ ; triangles,  $20 \text{ K min}^{-1}$ ).



**Figure 6.** Comparison of the activation energies found for the thermal decomposition of  $\text{Cu}_4\text{OC16}(\text{triphenylphosphine oxide})_4$  by the linear and nonlinear procedure.

the error of approximating the temperature integral increases with decreasing the  $x$  value. In particular at  $x \approx 50$  the ratio of  $|\delta E_\alpha/E_\alpha|$  to  $|\delta p(x)/p(x)|$  is about 0.02, whereas at  $x \approx 5$  it is about 0.13. In other words, we can normally expect that the approximation 6 of the temperature integral induces  $|\delta E_\alpha/E_\alpha|$  which is several times less than  $|\delta p(x)/p(x)|$ .

#### EXPERIMENTAL EXAMPLE

As an experimental example data<sup>15</sup> on the thermal decomposition of tetranuclear copper(II) complex of general formula  $\text{Cu}_4\text{OC16}(\text{triphenylphosphine oxide})_4$  have been taken. The process was studied by thermogravimetry in a nitrogen atmosphere at different heating rates. Figure 5 shows the plots of  $\alpha$  vs  $T_\alpha$  obtained for the second step of the decomposition which gives about 50% of the net mass loss. The conversion was computed as fractions of the net mass loss in this step. For isoconversional computations 40 equidistant values of conversion within the region 0.01–0.99 were chosen. The  $T_\alpha$  values related to these conversions were found by a nonlinear interpolation.

Unlike the model example which is a single-step reaction (Figure 2), the actual process of the thermal decomposition manifests a dependence of the activation energy upon conversion (Figure 6). This fact suggests that the process is a multistep reaction. A decrease in the effective activation energy is most likely caused by transition of the limiting

step from the high activation energy reaction to the low activation energy reaction.

Both the linear and nonlinear procedures show decreasing dependencies (from 75 to 55  $\text{kJ mol}^{-1}$ ) of the activation energy upon conversion (Figure 6). Taking into account that at  $10 \text{ K min}^{-1}$  the process occurs in the temperature region 630–830 K, the  $x$  value is expected to decrease from 14 to 8 with increasing conversion. In this case, the foregoing analysis (Figure 3) suggests that the deviation of the linearly estimated  $E_\alpha$  values from those evaluated with the nonlinear procedure should increase approximately from 0.9 to 2.3%. A comparison of the actual  $E_\alpha$  values really shows (Figure 6) a deviation which increases with increasing conversion. The  $H^-$  relative deviation of the linearly estimated  $E_\alpha$  value from that nonlinearly found increases from 0.9 to 2.2%.

#### CONCLUSIONS

The linear procedure may give quite satisfactory values of the activation energy at  $x > 13$ . The nonlinear procedure suggested in this paper shows extremely low errors in the activation energy which are practically independent of  $x$  value. Therefore, the nonlinear procedure can be recommended regardless of the  $x$  value to compute the activation energy required for predictions and for solving other problems sensitive to the accuracy of the activation energy.

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