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# Modification of the Integral Isoconversional Method to Account for Variation in the Activation Energy

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**ABSTRACT:** Integral isoconversional methods may give rise to noticeable systematic error in the activation energy when the latter strongly varies with the extent of conversion. This error is eliminated by using an integration technique that properly accounts for the variation in the activation energy. The technique is implemented as a modification of the earlier proposed advanced isoconversional method [Vyazovkin, S. J Comput Chem 1997, 18, 393]. The applications of the modified method are illustrated by simulations as well as by processing of data on the thermal decomposition of calcium oxalate monohydrate and ammonium nitrate. © 2000 John Wiley & Sons, Inc. J Comput Chem 22: 178–183, 2001

**Keywords:** kinetics; multistep reactions; condensed phase; activation energy

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## Introduction

The kinetics of many condensed phase reactions (e.g., decomposition, crystallization, polymerization, etc.) can be described by the following rate equation:<sup>1–3</sup>

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E}{RT}\right)f(\alpha) \quad (1)$$

where  $t$  is the time,  $\alpha$  is the extent of conversion,  $k(T)$  is the Arrhenius rate constant,  $A$  and  $E$  are the Arrhenius parameters (preexponential factor and activation energy, respectively),  $R$  is the gas con-

stant, and  $f(\alpha)$  is the reaction model associated with a certain reaction mechanism. Thermally stimulated reactions are commonly studied using linear heating program

$$\frac{dT(t)}{dt} = \beta \quad (2)$$

where  $\beta$  is the heating rate. A number of methods have been proposed for simultaneously estimating the values of  $E$  and  $A$ , and the reaction model from a single heating rate experiment.<sup>1,2</sup> In these methods, Arrhenius parameters are estimated by fitting data to various reaction models. Because in a single nonisothermal experiment  $T$  and  $\alpha$  are varied simultaneously, the model-fitting procedure allows errors in the functional form of the reaction model to be concealed by making compensating errors in  $k(T)$ .

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This mutual compensation of errors gives rise to the situation when almost any reaction model can satisfactorily fit data at the cost of estimating drastically different, but strongly correlated values of  $E$  and  $A$  (the so-called “kinetic compensation effect”).<sup>4</sup>

The uncertainty in estimating Arrhenius parameters is avoided in the isoconversional methods, which allow the model-fitting step to be eliminated by using multiple heating rate experiments. These methods are based on the isoconversional principle that states that the reaction rate at a constant extent of conversion is only a function of the temperature

$$\frac{d \ln(d\alpha/dt)_\alpha}{dT^{-1}} = -\frac{E_\alpha}{R} \quad (3)$$

(henceforth, the subscript  $\alpha$  indicates the values related to a given extent of conversion). The isoconversional methods permit the effective activation energy of a process to be unambiguously estimated as a function of the extent of conversion. Analysis of the resulting  $E_\alpha$  dependence may provide important clues about changes in reaction mechanism, if these changes are associated with changes in the activation energy.<sup>5</sup> However, some kinetic factors such as surface area of a reacting sample do not directly affect the activation energy, but the effective value of the preexponential factor. Therefore, additional kinetic information may be obtained using special techniques<sup>6,7</sup> for estimating the preexponential factor, whose value is also likely to vary with the extent of conversion. It is noteworthy that variable values of both effective activation energy and preexponential factor are not introduced artificially to accomplish a better data fit, but arise naturally from the application of the isoconversional methods.

By rearranging eq. (3), one can easily arrive at eq. (4)

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \text{Const} - \frac{E_\alpha}{RT} \quad (4)$$

which is the basis of the differential isoconversional method of Friedman.<sup>8</sup> Because this method employs instantaneous rate values, it is very sensitive to experimental noise, and tends to be numerically unstable, especially when the rate is estimated by numerical differentiation of experimental data. Another computational concern has been raised by Golikeri and Luss,<sup>9</sup> who theoretically demonstrated that the differential isoconversional method may yield the effective activation energy, which deviates largely from that of the individual reactions.

This situation is effectively avoided by using eq. (1) in its integral form

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^{t_\alpha} \exp\left(\frac{-E}{RT(t)}\right) dt = AJ[E, T(t_\alpha)] \quad (5)$$

where  $g(\alpha)$  is the integral form of the reaction model, and  $T(t)$  is the heating program. For a linear heating program [eq. (2)], the integral in eq. (5) can be replaced with various useful approximations<sup>1,2,10</sup> that may ultimately lead to simple linear equations for estimating the activation energy. For instance, the use Doyle's approximation<sup>11</sup> allows one to arrive at eq. (6)

$$\ln(\beta) = \text{Const} - \frac{E_\alpha}{RT_\alpha} \quad (6)$$

which is the basis of the integral isoconversional methods of Flynn and Wall<sup>12</sup> and Ozawa.<sup>13</sup> Equation (6) was derived assuming a constant activation energy.<sup>12</sup> This assumption obviously introduces some systematic error in estimating  $E_\alpha$ , if the latter varies with  $\alpha$ . This error does not appear in the differential isoconversional method of Friedman. For this reason one can estimate the systematic error of an integral isoconversional method by comparing it against the Friedman method. Because the latter is sensitive to experimental noise, this comparison is most effectively performed on simulated data that do not contain the noise.

Flynn and Wall<sup>12</sup> performed such a comparison for a simulated process that involves two competing and/or two independent reactions having activation energies 40 and 60 kcal mol<sup>-1</sup>, and found the integral [eq. (6)] and differential [eq. (4)] methods to yield similar results. A similar system of two reactions with activation energies 40 and 60 kcal mol<sup>-1</sup> were used by Dowdy,<sup>14</sup> who quantitatively compared the methods and estimated the systematic error of the integral method [eq. (6)] to be less than 4%. Burnham et al.<sup>15,16</sup> have applied both integral and differential isoconversional methods to a number of various decomposition processes. According to the results reported by these workers,<sup>15,16</sup> the difference in the activation energies determined by the integral and differential methods does not generally exceed 10%. Nevertheless, for the process of the thermal dehydration of calcium oxalate monohydrate, Budrugaec et al.<sup>17</sup> have found that the integral method gives rise to  $E_\alpha$  values that may deviate from the values obtained by the differential method by as much as 20%. Although this value seems to be more extreme than typical, we cannot

deny the fact that the systematic error of the integral method should necessarily increase with increasing the relative magnitude of the variation in  $E_\alpha$ . But does this fact invalidate the integral isoconversional methods in general? In this article we demonstrate that the integral methods are perfectly valid, if integration properly accounts for the variation in  $E_\alpha$  with  $\alpha$ . The method of such integration is described in the following section.

### Advanced Isoconversional Method

An advanced isoconversional method has been recently described by Vyazovkin in this journal.<sup>18</sup> As all other integral isoconversional methods, this method is based on the assumption that the reaction model,  $g(\alpha)$  is independent of the heating program,  $T(t)$ . By the virtue of this assumption, the  $J$ -integrals [eq. (5)] for any given value of  $\alpha$  are equal for all experiments, regardless of differences in the heating programs. This equality is equivalent to the condition of a minimum of the following function<sup>18</sup>

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (7)$$

where the subscripts  $i$  and  $j$  represent ordinal numbers of two experiments performed under different heating programs. Therefore  $E_\alpha$  is found as the value that minimizes  $\Phi(E_\alpha)$ .

The original method<sup>18</sup> [eq. (7)] uses the regular integration from 0 to  $t_\alpha$  [eq. (5)], as a result of which each value of  $E_\alpha$  becomes "averaged" over the region  $0 - \alpha$ , and the whole  $E_\alpha$  dependence undergoes an undesirable flattening. However, the method can be modified to adequately account for a variation of  $E_\alpha$  with  $\alpha$ . To do that, we replace the regular integration from 0 to  $t_\alpha$  [eq. (5)] with integration over small time segments as follows

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (8)$$

In eq. (8),  $\alpha$  varies from  $2\Delta\alpha$  to  $1 - \Delta\alpha$  with a step  $\Delta\alpha = (m + 1)^{-1}$ , where  $m$  is the number of the equidistant values of  $\alpha$  chosen for the analysis. As a result, the constancy of  $E_\alpha$  is assumed for only a small segment  $\Delta\alpha$ . The integral,  $J$  in eq. (8) is evaluated numerically from the experimental data by using the trapezoid rule.<sup>19</sup> The obtained values of the integral  $J$  are substituted in eq. (7), and minimization is carried out to find  $E_\alpha$ . Brent's algorithm<sup>19, 20</sup> of inverse quadratic interpolation is employed to find the minimum. The procedure is

repeated for each value of  $\alpha$  to find the dependence of the activation energy on the extent of conversion.

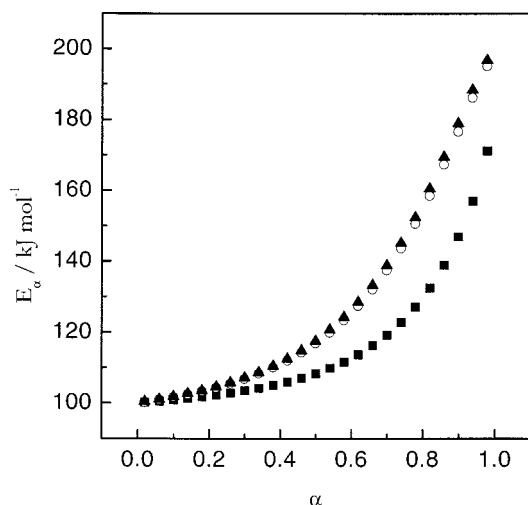
### Simulations

A strong variation in the effective activation energy may be observed for a process that involves two individual reactions each of which has a significantly different activation energy. A process that involves two parallel reactions of different reaction orders can be used to simulate this type of kinetics. The overall rate of this process is given as

$$\frac{d\alpha}{dt} = A_1 \exp\left(\frac{-E_1}{RT}\right)(1 - \alpha)^{n_1} + A_2 \exp\left(\frac{-E_2}{RT}\right)(1 - \alpha)^{n_2} \quad (9)$$

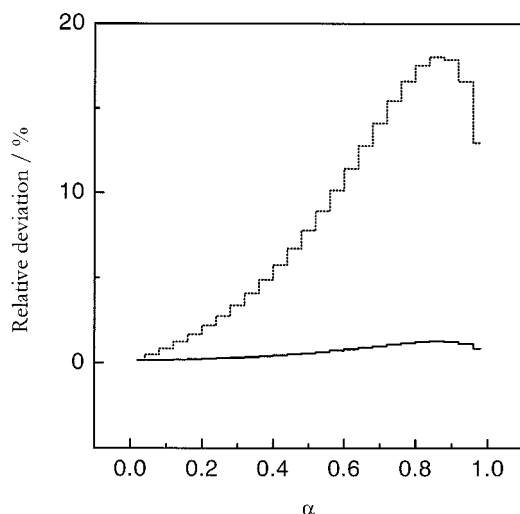
The parameters of eq. (9) have been set as follows:  $n_1 = 1$ ,  $E_1 = 200 \text{ kJ mol}^{-1}$ ,  $A_1 = 10^{16} \text{ min}^{-1}$ ,  $n_2 = 2$ ,  $E_2 = 100 \text{ kJ mol}^{-1}$ ,  $A_2 = 10^8 \text{ min}^{-1}$ . The process has been simulated at four linear heating rates [eq. (2)] of 1, 2, 4, and  $8^\circ\text{C min}^{-1}$ . The Runge-Kutta method of the fourth order<sup>19</sup> has been used to integrate eq. (9). Substitution of the obtained  $\alpha(t)$  data into eq. (9) gives the reaction rate as a function of time.

To apply the differential method of Friedman [eq. (4)], one has to determine the values of  $T_\alpha$  and  $(d\alpha/dt)$ . These values have been estimated from the simulated data via a nonlinear interpolation. Substitution of the obtained values into eq. (4) gives rise to the  $E_\alpha$  dependence shown in Figure 1. The nonlinear interpolation has also been employed to find the  $t_\alpha$  values to be used in the integral isoconversional method [eq. (7)]. Two different  $E_\alpha$  dependencies have been obtained by respectively using integration over the  $0 - t_\alpha$  [eq. (5)] and  $t_{\alpha-\Delta\alpha} - t_\alpha$  [eq. (8)] regions. The obtained dependencies are displayed in Figure 1, from which one can see that the use of the regular integration technique [eq. (5)] gives rise to the  $E_\alpha$  dependence, which deviates noticeably from the dependence estimated by the differential method [eq. (4)]. On the other hand, the modified integration technique [eq. (8)] yields the  $E_\alpha$  dependence, which is practically identical to that estimated by the differential method [eq. (4)]. The systematic error resulted from using the two integration techniques has been quantitatively estimated as the absolute relative deviation of the  $E_\alpha$  values estimated by the integral method from the  $E_\alpha$  values estimated by the differential method. The values of the absolute relative deviations are given



**FIGURE 1.**  $E_{\alpha}$  dependencies evaluated for the simulated process by different methods. Triangles: differential method [eq. (4)]; squares: integral method [eq. (7)] using regular integration [eq. (5)]; circles: integral method [eq. (7)] using modified integration [eq. (8)].

in Figure 2. It is seen that the use of the modified integration technique [eq. (8)] reduces the maximum deviation from 18% to about 1%. It can, therefore, be concluded that the modified integral isoconversional method is capable of providing valid values of the activation energy even if the latter demonstrates a strong variation with the extent of conversion.



**FIGURE 2.** Errors of the integral method associated with different integration techniques; dotted line: regular integration [eq. (5)]; solid line: modified integration [eq. (8)].

## Experimental Examples

In this section, we test the advanced isoconversional method [eq. (7)] against experimental data to compare the results of using the two different integration techniques [i.e., eqs. (5) and (8)]. As experimental examples, we have used the processes of the thermal decomposition of ammonium nitrate (AN) and of thermal dehydration of calcium oxalate monohydrate (COM). The kinetics of both processes have been extensively studied.<sup>1,2</sup> The thermal decomposition of AN is characterized by a practically constant activation energy ( $\sim 90 \text{ kJ mol}^{-1}$ ).<sup>21</sup> For the thermal dehydration of COM, several workers have reported (c.f., our recent review<sup>5</sup> and references therein) a significant decrease (from  $\sim 200$  to  $\sim 80 \text{ kJ mol}^{-1}$ ) in the effective activation energy with the extent of reaction. The decrease is consistent with the kinetic model proposed by Pavlyuchenko and Prodan,<sup>22,23</sup> who have shown that the effective activation energy of a reversible decomposition is given as

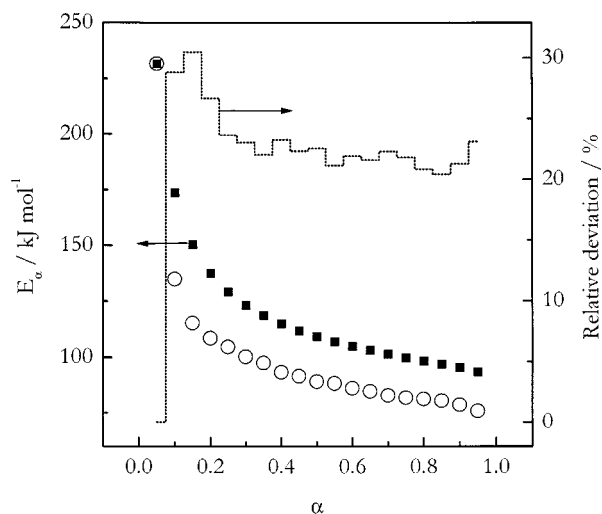
$$E_{ef} = E_2 - \lambda + mQ \frac{P_0^m}{P_0^m - P^m} \quad (10)$$

where  $E_2$  is the activation energy of the reverse reaction,  $\lambda$  is the heat of adsorption,  $m$  is a constant ( $0 < m < 1$ ),  $Q$  is the thermal effect of reaction,  $P_0$  is the equilibrium pressure, and  $P$  is the partial pressure of the gaseous product. Under the rising temperature conditions the value of  $P_0$  continuously increases that causes the last term of the sum in eq. (10) to decrease. Because the initial stages of a reversible dehydration occur not far from equilibrium (i.e.,  $P \approx P_0$ ), they are characterized by a great value the effective activation energy, which decreases at the later stages as the system departs from equilibrium (i.e.,  $P \ll P_0$ ). The two aforementioned processes have been chosen because they present two rather extreme situations, and, therefore, their analysis may provide realistic estimates for most practical cases that are likely to fall in between.

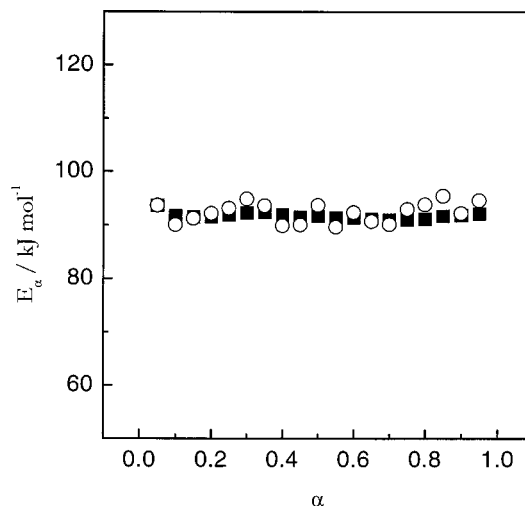
Thermogravimetric analysis (TGA) provides a convenient means to monitor the kinetics of the above-mentioned processes by measuring the mass loss as a function of time. AN 99.8% purity (Mallinckrodt) and COM >98% purity (Fluka) were used with no further purification. The samples were ground in an agate mortar. The particle size was  $< 300 \mu\text{m}$ , as measured using an optical microscope. A Mettler-Toledo TGA/SDTA851<sup>e</sup> module was used to measure the mass loss kinetics. AN samples of  $\sim 1 \text{ mg}$  were placed in open  $40\text{-}\mu\text{L}$  Al

pans and heated at five heating rates of 2.5, 5, 7.5, 10, and 12.5°C min<sup>-1</sup>. For dehydration of COM we used ~10 mg to keep the mass loss during dehydration around 1 mg. COM samples were heated in open 40- $\mu$ L Al pans at five heating rates of 1, 2, 5, 10, and 20°C min<sup>-1</sup>. All runs were conducted in an atmosphere of nitrogen at a flow rate of 70 mL min<sup>-1</sup>.

The values of  $\alpha$  have been determined from the TGA data as partial mass losses. Determination of the  $t_\alpha$  values has been described in the previous section. The  $E_\alpha$  dependencies produced from the obtained experimental data are shown in Figures 3 and 4. The thermal dehydration of COM demonstrates a strong variation of the activation energy with the extent of dehydration (Fig. 3). Because the modified integration technique [eq. (8)] has been found to give rise to valid  $E_\alpha$  values, they can be used to estimate a systematic error of the regular integration technique [eq. (5)]. It is seen from Figure 3 that this error, estimated as an absolute relative deviation, may exceed 20%. The thermal dehydration of COM presents the extreme example when a variation in  $E_\alpha$  is comparable to the medium value of  $E_\alpha$ . A similar situation has been observed for the simulated data (Fig. 2) for which the error is also close 20%. These values appear to be the "worst-case scenario" estimate for the systematic error of an integral isoconversional method, whose integration procedure does not account for a variation of the activation energy with the extent of conversion.



**FIGURE 3.**  $E_\alpha$  dependencies evaluated for the thermal dehydration of COM by the integral method [eq. (7)] when using regular (squares) and modified (circles) integration techniques. Dotted line represents the systematic error of the regular integration technique.



**FIGURE 4.**  $E_\alpha$  dependencies evaluated for the thermal decomposition of AN by the integral method [eq. (7)] when using regular (squares) and modified (circles) integration techniques.

For the thermal decomposition of AN the activation energy does not practically vary with the extent of conversion (Fig. 4). In this case, both regular [eq. (5)] and modified [eq. (8)] integration techniques lead to almost identical  $E_\alpha$  dependencies. Note that the use of the modified technique gives rise to a slightly larger scatter in the  $E_\alpha$  values. This happens because the modified integration technique necessarily involves a fewer number of points than the regular technique in which the number of points involved in numerical integration steadily increases with  $\alpha$ . Nevertheless, the somewhat lower precision of numerical integration is only a small price to pay for eliminating significant systematic errors associated with the regular integration technique.

## Conclusions

Integral isoconversional methods may give a noticeable systematic error in the value of the activation energy, when the latter significantly varies with the extent of conversion. This error may exceed 20% in the case when the magnitude of the variation is comparable to the medium value of the activation energy. This error is eliminated by using an integration technique that accounts for the variation in the activation energy with the extent of conversion. This technique has been incorporated into the earlier proposed advanced isoconversional method.



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