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Estimating Realistic Confidence Intervals for the Activation Energy Determined from Thermoanalytical Measurements

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A statistical procedure is proposed for estimating realistic confidence intervals for the activation energy determined by using an advanced isoconversional method. Nine sets of five thermogravimetric measurements have been produced for the process of gassification of ammonium nitrate at five different heating rates. Independent estimates of the confidence intervals for the activation energy have been obtained from these data sets. Agreement with these independent estimates demonstrates that the proposed statistical procedure is capable of adequately estimating the actual uncertainty in the activation energy determined from a small number of measurements. The resulting averaged relative errors in the activation energy were found to be 26, 21, and 17% for three, four, and five heating rate estimates, respectively.

Thermoanalytical methods find extensive application in analysis of various materials.^{1,2} The field of analytical applications constantly expands by accommodating new technical solutions.^{3–7} In particular, thermal methods of analysis are effectively used to study the kinetics of chemical reactions.^{1,2,8} These studies usually have two major objectives, namely, probing the reaction mechanisms and parametrizing the reaction rates. Of these two objectives, the latter has the foremost practical importance, because kinetic parameters are routinely used for predicting thermal stability of materials. In this circumstance, one is primarily interested in the effect of temperature that is traditionally parametrized via the Arrhenius equation

$$k(T) = A \exp(-E/RT) \quad (1)$$

where $k(T)$ is the rate constant at a temperature, T , R is the gas constant, and A and E are Arrhenius parameters, the preexpo-

nential factor and the activation energy, respectively. Because the temperature sensitivity of the reaction rate is predominantly determined by the activation energy, obtaining realistic estimates for this parameter is critical for predicting thermal stabilities.⁹ Chemometrics offers a wealth of statistical techniques for estimating parameters and their confidence intervals as they pertain to various chemical problems.^{10,11}

A widely used method of estimating the activation energy by fitting various reaction models to single heating rate data results in a large uncertainty that originates primarily from the uncertainty of choosing the appropriate reaction model. This uncertainty is eliminated when model-free isoconversional methods are used. In this paper, we propose a statistical procedure for estimating confidence intervals for the activation energy evaluated by the use of an advanced isoconversional method,¹² which has been successfully applied to thermoanalytical data to elucidate the kinetics and mechanism of processes occurring in inorganic and polymeric materials.^{13–15} The proposed statistical procedure is validated by applying traditional and robust statistical techniques to a series of independent experimental measurements.

EXPERIMENTAL SECTION

As an experimental subject we used ammonium nitrate, which undergoes complete gassification on heating. Thermogravimetric analysis (TGA) provides a convenient means to monitor the kinetics of this process by measuring the mass loss as a function of time. Ammonium nitrate (AN; 99.8% purity, Mallinckrodt) was used with no further purification. The samples were ground up in an agate mortar. The particle size was $<300 \mu\text{m}$ as measured by using an optical microscope. A Mettler-Toledo TGA/SDTA851e 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 $12.5 \text{ }^\circ\text{C min}^{-1}$. These five experiments were run nine times in order to produce nine inde-

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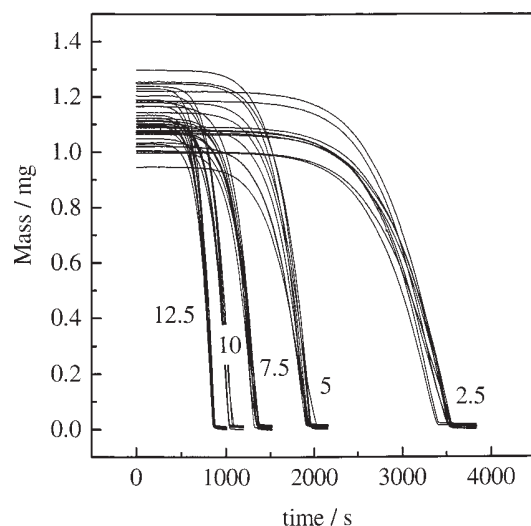


Figure 1. Mass loss kinetic curves obtained at different heating rates. The heating rate of an experiment (in °C min⁻¹) is indicated by each series of curves.

pendent sets of data for the purpose of validating the proposed statistical procedure. All runs were conducted in a flowing atmosphere of nitrogen at a flow rate 70 mL min⁻¹. The resulting kinetic curves are shown in Figure 1.

SINGLE AND MULTIPLE HEATING PROGRAM METHODS

Kinetic analysis of solid-state decompositions is usually based on a single-step kinetic equation^{16,17}

$$d\alpha/dt = k(T) f(\alpha) \quad (2)$$

where t is the time, α is the extent of conversion, and $f(\alpha)$ is the reaction model associated with a certain decomposition mechanism. At any moment of time, TGA allows one to determine α as a partial mass loss. The direct application of eq 2 to TGA data requires numerical differentiation of experimental measurements. However, this procedure typically produces unacceptably noisy data. This situation is effectively avoided by using eq 2 in its integral form

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^{t_\alpha} \exp\left(\frac{-E}{RT(t)}\right) dt = A[J(E, T(t_\alpha))] \quad (3)$$

where $T(t)$ is the heating program and $g(\alpha)$ is the integral form of the reaction model. Henceforth, the subscript α denotes the values related to a given extent of conversion. Depending on the reaction mechanism, the reaction model may take various forms,^{16,17} some of which are shown in Table 1. Thermoanalytical runs are commonly carried out under linear heating rate

$$dT(t)/dt = \beta \quad (4)$$

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Table 1. Activation Energies for Decomposition of AN at 5 °C min⁻¹ Determined Using the Coats–Redfern Eq 5

<i>N</i>	reaction model	$g(\alpha)$	$E/\text{kJ mol}^{-1}$	$ r $
1	power law	$\alpha^{1/4}$	11.5 ± 0.1	0.9670
2	power law	$\alpha^{1/3}$	17.7 ± 0.2	0.9749
3	power law	$\alpha^{1/2}$	30.1 ± 0.3	0.9803
4	power law	$\alpha^{3/2}$	104.5 ± 0.8	0.9851
5	1-D diffusion	α^2	141.6 ± 1.0	0.9856
6	Mampel (first order)	$-\ln(1 - \alpha)$	81.5 ± 0.6	0.9824
7	Avrami–Erofeev	$[-\ln(1 - \alpha)]^{1/4}$	15.1 ± 0.2	0.9722
8	Avrami–Erofeev	$[-\ln(1 - \alpha)]^{1/3}$	22.5 ± 0.2	0.9766
9	Avrami–Erofeev	$[-\ln(1 - \alpha)]^{1/2}$	37.2 ± 0.3	0.9799
10 ^a	3-D diffusion	$[1 - (1 - \alpha)^{1/3}]^2$	156.7 ± 1.0	0.9875
11 ^a	contracting sphere	$1 - (1 - \alpha)^{1/3}$	74.8 ± 0.5	0.9865
12 ^a	contracting cylinder	$1 - (1 - \alpha)^{1/2}$	72.4 ± 0.5	0.9866

^a Statistically equivalent models.

where β is the heating rate. For this case, the integral in eq 3 can be replaced with various useful approximations^{16–18} that may ultimately lead to simple linear equations to estimate Arrhenius parameters. One such approximation gives rise to the popular Coats–Redfern equation¹⁹

$$\ln\left[\frac{g_j(\alpha)}{T^2}\right] = \ln\left(\frac{A_j R}{\beta E_j}\right) \left(1 - \frac{2R\bar{T}}{E_j}\right) - \frac{E_j}{RT} \quad (5)$$

where \bar{T} is the mean experimental temperature. The subscript j has been introduced to emphasize that substituting a particular reaction model into eq 5 results in evaluating the corresponding Arrhenius parameters. This equation as well as a number of other similar equations is customarily used for kinetics analysis of thermoanalytical measurements conducted at a single heating rate. Arrhenius parameters and their respective confidence intervals are then estimated with the help of the standard statistical procedure of linear regression analysis.¹¹ Table 1 provides a representative example of this type of kinetic analysis as applied to the process of gassification of AN. Note that the confidence intervals for the activation energy are very small. This is quite typical for kinetic analyses that use fitting of various reaction models to single heating rate data. But do these small confidence intervals reflect the actual uncertainty in estimating the activation energy?

As seen from Table 1, the value of the activation energy strongly depends on the choice of the reaction model. The choice of the “best” model is usually based on a statistical characteristic such as a coefficient of linear correlation, r . The “best” linearity is accomplished for the reaction model 10 (Table 1), which is characterized by the maximum absolute value of r , r_{\max} . A statistical test based on Fisher’s transformation allows one to easily verify whether the other values of r differ significantly (i.e., with 95% confidence) from r_{\max} .¹¹ By applying this test we find that the reaction models 10–12 are statistically equivalent descriptions of the process. However, the use of the model 10 results in the

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activation energy that is more than 2 times greater (157.6 versus 72.4 and/or 74.8 kJ mol⁻¹) than the value obtained by using the model 11 or 12. This dramatic difference reflects the actual uncertainty in estimating the activation energy. Therefore, for the methods that use fitting of various reaction models to single heating rate data, the uncertainty in estimating the activation energy primarily originates from the uncertainty of choosing the reaction models.

This type of uncertainty is eliminated when model-free isoconventional methods of kinetic analysis are used.²⁰ Flynn and Wall²¹ and Ozawa²² developed first integral isoconventional methods for evaluating the activation energy from a series of thermoanalytical experiments conducted at several heating rates. These methods assume that the reaction model, $g(\alpha)$ is independent of the heating rate. The analysis of measurements related to a given extent of conversion at different heating rates allows one to eliminate the analytical form of the reaction model from evaluations of the activation energy. Vyazovkin¹² proposed an advanced isoconventional method which is based on the assumption that the reaction model is independent of the heating program, $T(t)$. According to this method, for a set of n experiments carried out at different heating programs, the activation energy is determined at any particular value of α by finding E_α , which minimizes the function

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J(E_\alpha, T_i(t_\alpha))}{J(E_\alpha, T_j(t_\alpha))} \quad (6)$$

where the subscripts i and j represent ordinal numbers of two experiments performed under different heating programs. The integral, J in eq 6 is evaluated numerically from the experimental data by using the trapezoid rule. The minimization procedure is repeated for each value of α to find the dependence of the activation energy on the extent of conversion. An advantage of the advanced isoconventional method is that it can be applied to study the kinetics under arbitrary temperature programs such as distorted linear (e.g., self-heating/cooling) or purposely nonlinear (e.g., temperature modulations) heating. Most recently, the method has been modified to more adequately account for a strong variation of the activation energy with the temperature. This is accomplished by performing integration as follows

$$J(E_\alpha, T_i(t_\alpha)) \equiv \int_{t_{\alpha, m-1}}^{t_{\alpha, m}} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (7)$$

where m varies from 1 to the number of the equidistant values of α chosen for the analysis (typically 5–50).

CONFIDENCE INTERVALS FOR THE ADVANCED ISOCONVENTIONAL METHOD

By virtue of the basic assumption that the reaction model, $g(\alpha)$, is independent of the heating program, $T(t)$, the J integrals (eq 7) for any particular segment ($t_{\alpha, m-1}$ – $t_{\alpha, m}$) should be equal for all experiments, regardless of differences in the heating programs

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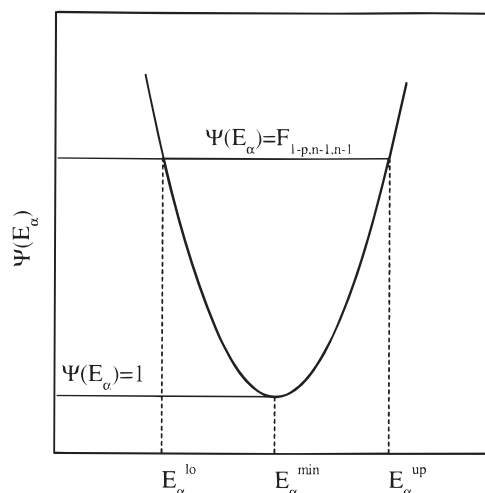


Figure 2. Illustration of the statistical procedure of estimating the Fisher confidence limits.

(cf. eq 3). Therefore, the ratio of any two of the J integrals should be unity in an ideal situation. It is noteworthy that for any set of n experiments, the total number of terms contributing to the double summation (eq 6) is $n(n-1)$. Then the following variance

$$S^2(E_\alpha) = \frac{1}{n(n-1)} \sum_{i=1}^n \sum_{j \neq i}^n \left(\frac{J(E_\alpha, T_i(t_\alpha))}{J(E_\alpha, T_j(t_\alpha))} - 1 \right)^2 \quad (8)$$

should be independent of the number of experiments performed (aside from the natural fluctuations associated with experimental values themselves). Minimization of this variance yields an optimum value of the activation energy, E_{\min} , which is characterized by the minimum variance, S_{\min}^2 . Then, statistics constructed as

$$\Psi(E_\alpha) = S^2(E_\alpha) / S_{\min}^2 \quad (9)$$

have the F distribution.¹¹ This enables the confidence limits for E_{\min} to be found by estimating the confidence limits for the variance S_{\min}^2 . The $p \times 100\%$ confidence interval for S_{\min}^2 can be determined from the following condition

$$\Psi(E_\alpha) < F_{1-p, n-1, n-1} \quad (10)$$

where $F_{1-p, n-1, n-1}$ is a percentile of the F distribution for $(1-p) \times 100\%$ confidence probability. Then for E_{α}^{\min} , we can estimate the lower and upper confidence limit, (E_{α}^{lo} and E_{α}^{up} , respectively) as the values of E_α for which $\Psi(E_\alpha) = F_{1-p, n-1, n-1}$ (Figure 2).

VALIDATION OF THE STATISTICAL PROCEDURE

To obtain a single value of E_α from eq 8, one needs a set of α versus t data obtained at several different heating programs. The kinetics of gassification of AN have been measured at five heating rates (2.5, 5, 7.5, 10, and 12.5 °C min⁻¹). The first three, four, and then all five heating rates have been respectively used to obtain three, four, and five heating rate estimates of E_α . Because the measurements have been performed nine times, we have nine independent sets of experimental measurements obtained at the

five heating rates. This allows us to obtain nine independent three, four, and five heating rate estimates for each given value of E_a . The nine independent estimates of $E_{a,i}$ ($i = 1, \dots, 9$) have been used to estimate the actual confidence intervals. Two different statistical procedures have been employed to evaluate these confidence intervals from $E_{a,i}$. First, we estimated the mean value of $E_{a,i}$ and its 95% confidence interval by using Student's statistics.¹¹ The resulting confidence intervals are further referred as "Student's confidence intervals" and denoted as $\Delta_S E_a$.

Note that the Student estimates are based on the normal distribution of the population. However, the true distribution of the population $E_{a,i}$ is unknown. For this reason, we have also used a robust (i.e., distribution-free) statistical procedure that employs the median.¹¹ In a population arranged in ascending order $X_1 < X_2 < \dots < X_m$, the median is a value such that half of the X_i values are above and half below it. In the ordered population $E_{a,1}, \dots, E_{a,9}$, the median is $E_{a,5}$. Confidence limits for the median can be determined as X_r^* and X_{m-r+1}^* , where $r = 1, \dots, m-1$. The probability that the median is greater than X_r^* but less than X_{m-r+1}^* can be evaluated as²³

$$P \geq 2^{-m} \sum_{i=r}^{m-r} \frac{m!}{i!(m-i)!} \quad (11)$$

The interval (X_r^*, X_{m-r+1}^*) can be used as a $100 \times P\%$ confidence interval for the median. Equation 11 suggests that for the median of the population $E_{a,1}, \dots, E_{a,9}$ the values $E_{a,2}$ and $E_{a,8}$ are 96% confidence limits. Because the values of $E_{a,i}$ vary discretely, we cannot determine the 95% confidence limits exactly. However, the 96% confidence limits are close enough for a practical comparison to be made. Because the median $E_{a,5}$ was found to be insignificantly different from the midpoint between $E_{a,2}$ and $E_{a,8}$, we have determined the confidence interval as

$$\Delta_M E_a = (E_{a,8} - E_{a,2})/2 \quad (12)$$

The resulting confidence intervals are further referred as "median confidence intervals".

Estimating $\Delta_S E_a$ and $\Delta_M E_a$ is an experimentally laborious and, thus, impractical procedure that requires obtaining the sets of recurring measurements. A practical procedure should afford estimating the confidence intervals for a single set of experimental measurements. Such a procedure has been described in the previous section (cf. eqs 8–10 and Figure 2). The application of this procedure to the nine independent sets of measurements results in obtaining nine independent pairs of the confidence limits, $E_{a,i}^{\text{lo}}$ and $E_{a,i}^{\text{up}}$. Since the values $E_{a,i}^{\text{min}}$ are positioned near the midpoint between $E_{a,i}^{\text{lo}}$ and $E_{a,i}^{\text{up}}$, the confidence intervals for $E_{a,i}^{\text{min}}$ have been estimated as follows

$$\Delta_F E_{a,i} = (E_{a,i}^{\text{up}} - E_{a,i}^{\text{lo}})/2 \quad (13)$$

Because a single $\Delta_F E_{a,i}$ value may happen to be an outlier, the values have been averaged over the nine independent measure-

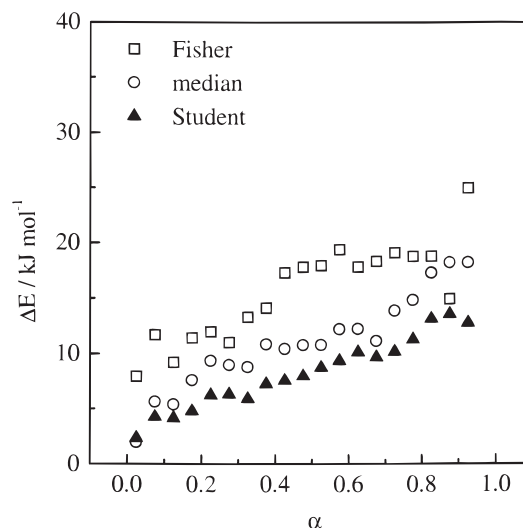


Figure 3. Comparison of Fisher confidence intervals with independently estimated median and Student confidence intervals for five heating rate estimates.

ments and replaced with the mean, $\overline{\Delta_F E_a}$, which has been used for comparison purposes. The resulting confidence intervals are further referred to as "Fisher confidence intervals" to emphasize the fact that they have been evaluated by utilizing Fisher's F statistics. Now, if the proposed statistical procedure (eqs 8–11) is valid, then the values of $\overline{\Delta_F E_a}$ should be consistent with the independently obtained estimates $\Delta_S E_a$ and $\Delta_M E_a$. The comparison is given in the following section.

RESULTS AND DISCUSSION

The proposed statistical procedure (eqs 8–10) has been applied to the nine sets of AN gassification data to obtain three, four, and five heating rate estimates for the activation energies and the respective Fisher confidence intervals. The computations have been carried out for 20 intervals of the extent of reaction ($\alpha = 0.025$ – 0.975 with a step 0.050). The obtained values of $\overline{\Delta_F E_a}$ have been compared against the independently determined the Student ($\Delta_S E_a$) and median ($\Delta_M E_a$) confidence intervals for three, four, and five heating rate estimates. In all three cases, the Student confidence intervals are somewhat smaller than the median confidence intervals (cf. Figure 3). Because the latter are robust and more conservative, it appears to be reasonable to rely on them for comparison purposes. In the case of the three and four heating rates, the Fisher confidence intervals have been practically identical with the independently estimated median confidence intervals. In the case of the five heating rate estimates (Figure 3), the Fisher confidence intervals seem to be slightly larger, which may simply be due to the presence outliers among the $\Delta_F E_{a,i}$ values (eq 13). At any rate, in all three cases, the Fisher confidence intervals estimated by using the proposed statistical procedure (eqs 8–10) are either consistent or more conservative than the independently determined median and Student confidence intervals. Therefore, the statistical procedure proposed in this work gives rise to the confidence intervals, which are realistic measures of the actual scatter in the activation energies determined by the isoconversional method.

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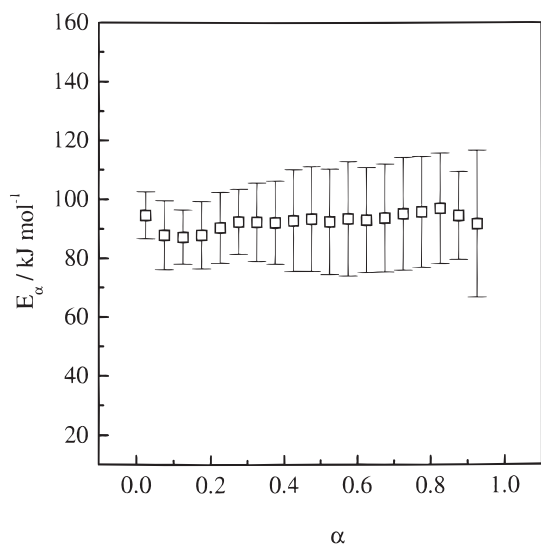


Figure 4. Activation energy and Fisher confidence intervals averaged over nine independent five heating rate estimates.

Let us now evaluate the Fisher confidence intervals in terms of the relative error in the activation energy. To do that we use the mean Fisher confidence interval $\Delta_F E_{\alpha}$ and the mean activation energy \overline{E}_{α} obtained as an average of the nine independent values of $E_{\alpha,i}$. Figure 4 demonstrates the values obtained for five

heating rate estimates. Then we estimated the ratio of $\overline{\Delta_F E_{\alpha}}$ to \overline{E}_{α} and averaged it over the number of the E_{α} values. The resulting averaged relative error in the activation energy was found to be 26, 21, and 17% for three, four, and five heating rate estimates, respectively. These errors may appear somewhat greater than one would wish for, but they are significantly smaller than the actual uncertainty in the activation energies estimated by fitting various reaction models to single heating rate data (cf. Table 1 and other examples in our recent review²⁰).

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