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TWO TYPES OF UNCERTAINTY IN THE VALUES OF ACTIVATION ENERGY

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> *'When you're buying a bird, make sure it hasn't got teeth. If it's got teeth, it isn't a bird.'*
> *Daniil Kharms*

Abstract

The activation energies of the same process are often reported to have different values, which are usually explained by the differences in experimental conditions and sample characteristics. In addition to this type of uncertainty, which is associated with the process ($\Delta E_{\text{process}}$) there is an uncertainty related to the method of computation of the activation energy (ΔE_{method}). For a method that uses fitting single heating rate data to various reaction models, the value of ΔE_{method} is large enough to explain significant differences in the reported values of the activation energy. This uncertainty is significantly reduced by using multiple heating rate isoconversional methods, which may be recommended for obtaining reference values for the activation energy.

Keywords: activation energy, ammonium nitrate, reaction kinetics, solid state, thermal decomposition

Introduction

One of the primary objectives of kinetic analysis is parameterizing the temperature dependence of the reaction rate. This dependence is usually described by the Arrhenius equation

$$k(T)=A\exp\left(\frac{-E}{RT}\right) \tag{1}$$

where *k(T)* is the rate constant at a temperature, T, R is the gas constant, and A and E are Arrhenius parameters, the preexponential factor and the activation energy, respectively. Although both Arrhenius parameters are needed to describe the temperature dependence, the discussion of the reaction kinetics traditionally tends to be focused on the activation energy (e.g., Galwey and Brown [1]). There seem to be two major reasons for that. Firstly, the temperature sensitivity of the reaction rate is predominantly determined by the activation energy, whereas the preexponential factor plays the role of a scaling parameter, which determines the absolute value of the reac-

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tion rate. Secondly, the preexponential factor is strongly correlated with the activation energy via a compensation effect [2], which makes the preexponential factor a dependent and, therefore, inferior parameter. The focus of the present paper is also on the activation energy. In this paper, we briefly discuss the sources of uncertainty in the experimental value of the activation energy.

Two sources of uncertainty in the activation energy

The reactions of solids usually involve multiple steps of both chemical (e.g., nucleation and nuclei growth) and physical (e.g., diffusion, sublimation, adsorption, and desorption) nature. Thermal analysis methods, such as TG and DSC, measure the overall reaction rate, which is composed of the rates of the individual steps. The contribution of these steps to the overall rate may depend strongly on experimental factors, such as pressure and temperature, and/or on sample characteristics, such as mass or particle size. Because the individual reaction steps are likely to have different activation energies, the effective activation energy determined from thermal analysis measurements may differ noticeably for various experimental conditions and sample characteristics. This fact has been repeatedly stressed by Maciejewski [3, 4], who suggests that the activation energies of a solid state process should necessarily be compared with regard to experimental conditions and sample characteristics.

When studying the same process, different workers usually use different experimental conditions and samples. These differences cause fluctuations in the process that ultimately gives rise to an uncertainty in the experimental value of the activation energy. Note that this type of uncertainty is associated with the process itself. We denote this uncertainty as $\Delta E_{\mathrm{process}}$. This type of uncertainty is most frequently used to explain the difference in the E values reported by different workers for the same process.

Experimental conditions and sample characteristics are, however, not the only source of the uncertainty in the experimental activation energy. Another important source is the method of estimating the activation energy. Generally, the uncertainty in the activation energy may be presented as the sum

$$\Delta E = \Delta E_{\mathrm{process}} + \Delta E_{\mathrm{method}} \qquad (2)$$

where $\Delta E_{\mathrm{method}}$ represents the uncertainty related to the computational methods. The latter can be conventionally separated in two categories. The first category involves the methods that allow the activation energy to be estimated from the data of a single heating rate experiment. The second category of the methods makes use of data sets obtained at multiple heating rates. In the following sections we use earlier obtained [5] experimental data on the thermal decomposition of ammonium nitrate (AN) to estimate $\Delta E_{\mathrm{method}}$ for some methods of these two categories.

$\Delta E_{\mathrm{method}}$ for single heating rate methods

A typical representative of the single heating rate methods is the Coats–Redfern method [6], which uses Eq. (3)

$$\ln\left[\frac{g_{\mathrm{j}}(\alpha)}{T^2}\right]=\ln\left(\frac{A_{\mathrm{j}}R}{\beta E_{\mathrm{j}}}\right)\left(1-\frac{2R\overline{T}}{E_{\mathrm{j}}}\right)-\frac{E_{\mathrm{j}}}{RT} \tag{3}$$

to determine Arrhenius parameters. In Eq. (3), $g(\alpha)$ is the reaction model (Table 1), β is the heating rate, and $\overline{T}$ is the mean experimental temperature. The subscript j has been introduced to emphasize that substituting a particular reaction model into Eq. (3) results in evaluating the corresponding Arrhenius parameters. Because the left-hand side of Eq. (3) is a linear function of the reciprocal temperature, one can apply the standard statistical procedure of linear regression analysis [7] to estimate Arrhenius parameters and their respective confidence intervals.

Table 1 provides a representative example of this type of kinetic analysis as applied to the data on the thermal decomposition of AN. Note that the confidence intervals for the activation energy are very small. This is quite typical for the methods that use fitting of single heating rate data to various reaction models. But do these small confidence intervals reflect the actual uncertainty in estimating the activation energy?

Table 1 Activation energies for decomposition of AN at 5°C min^{-1} determined using the Coats–Redfern Eq. (3)

N	Reaction model	$g(\alpha)$	E/kJ mol^{-1}	$\lvert r \rvert$
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	One-dimensional 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]	Three-dimensional 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

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 N 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 if the other values of r differ significantly from $r_{\max}$ [7, 8]. By applying this test we find that the reaction models 10, 11, and 12 are statistically equivalent descriptions of the process. However, the use of model 10 results in the activation energy that is more than two times greater (156.7 *vs.* 72.4 and/or 74.8 kJ mol^{-1}) than the value obtained by using 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 (i.e., ΔE_{method}) primarily originates from the uncertainty of choosing the reaction models.

Unfortunately, it is not very common to perform the proper statistical analysis that allows one to identify statistically equivalent reaction models. More commonly one would simply choose the 'best' model, which is characterized by the maximum absolute value of a correlation coefficient. For the thermal decomposition of AN such model is N 10, and the respective value of the activation energy is 156.7±1.0 kJ mol^{-1}. Therefore, this value is quite likely to be reported as the activation energy of the process.

ΔE_{method} for multiple heating rate methods

The most common representatives of the multiple heating rate methods are isoconversional methods [9–11]. 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

$$\frac{\mathrm{d}\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha}}{\mathrm{d}T^{-1}}=-\frac{E_{\alpha}}{R} \tag{4}$$

(henceforth the subscript α indicates the values related to a given extent of conversion). As seen from Eq. (4), the analysis of measurements related to a given extent of conversion at different heating rates allows one to eliminate the procedure of choosing the reaction model and, therefore, the related uncertainty from evaluations of the activation energy.

Vyazovkin [12] proposed an advanced isoconversional method which 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. 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

$$\Phi(E_{\alpha})=\sum_{\mathrm{i}=1}^{\mathrm{n}}\sum_{\mathrm{j}\neq\mathrm{i}}^{\mathrm{n}}\frac{J[E_{\alpha},T_{\mathrm{i}}(t_{\alpha})]}{J[E_{\alpha},T_{\mathrm{j}}(t_{\alpha})]} \tag{5}$$

where the subscripts *i* and *j* represent ordinal numbers of two experiments performed under different heating programs, *T(t)*. Most recently, the method has been modified [13] to more adequately account for a strong variation of E_α with α. This is accomplished by performing integration over small time segments as follows

$$J[E_\alpha, T(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT(t)}\right]\mathrm{d}t \qquad (6)$$

In Eq. (6), α varies from $\Delta\alpha$ to $1-\Delta\alpha$ with a step $\Delta\alpha=(m+1)^{-1}$, where *m* is the number of the equidistant values of α chosen for the analysis. Confidence inervals for E_α are estimated by using a special statistical procedure [5].

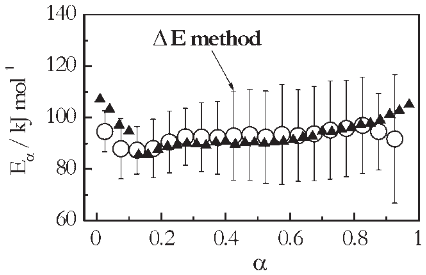

Fig. 1 Activation energies for the thermal decomposition of AN studied by Vyazovkin and Wight (○) [5] and Koga and Tanaka (▲) [14]. For better resolution, the values reported by Koga and Tanaka are shown with a larger α-step than in the original publication

Figure 1 displays the values of E_α and respective confidence intervals estimated for the thermal decomposition of AN. The confidence intervals are 10–20% of the E_α value and represent the uncertainty in the activation energy ($\Delta E_{\mathrm{method}}$) determined by the advanced isoconversional method. Because the E_α values are practically independent of α (Fig. 1), one is likely to report the mean value of the activation energy 92.6±1.3 kJ mol^{-1}.

$\Delta E_{\mathrm{method}}$ *vs.* $\Delta E_{\mathrm{process}}$

As shown above, the application of single and multiple heating rate methods to the data on the thermal decomposition of AN is likely to result in the reporting of two different values of the activation energy, which are, respectively, 156.7±1.0 and 92.6± 1.3 kJ mol^{-1}. Let us compare each of these values against the value reported by Koga and Tanaka [14], who studied the thermal decomposition of AN under conditions that are obviously not identical to those used in our study (Table 2). To evaluate the activation energy, Koga and Tanaka also employed a multiple heating rate isoconversional method. They obtained E_α values which, with regard to the error bars (i.e., $\Delta E_{\mathrm{method}}$) are indistinguishable from our values (Fig. 1). The mean activation energy is

93.3±1.0 kJ mol^{-1} which agrees very well with our mean value, despite the difference in experimental condtions used in the two studies (Table 2). This suggests, that for these two studies, the value of $\Delta E_{\mathrm{process}}$ is smaller than $\Delta E_{\mathrm{method}}$ associated with the isoconversional method.

Table 2 Experimental conditions and sample characteristics for the thermal decomposition of AN conducted in two different studies

Experimental	Study	
	Koga and Tanaka [14]	Vyazovkin and Wight [5]
AN vendor	Katayama	Mallinckrodt
Sample mass	10 mg	1 mg
Pan material	Pt	Al
TG manufacturer	Shimadzu	Mettler-Toledo
Heating rate	0.5–10°C min^{-1}	2.5–12.5°C min^{-1}
Purge gas	N_2	N_2
Purge gas flow rate	30 ml min^{-1}	80 ml min^{-1}

The value obtained by the single heating rate method (156.7±1.0 kJ mol^{-1}) is distinctly different from the value of the mean activation energy (93.3±1.0 kJ mol^{-1}) derived from the data by Koga and Tanaka. Without performing the proper statistical analysis (see above), the actual uncertainty would remain unknown, and the confidence interval ±1.0 kJ mol^{-1} would be mistaken for the value of $\Delta E_{\mathrm{method}}$ for the single heating rate method. In this circumstance, the difference in the activation energies (156.7±1.0 *vs.* 93.3±1.0 kJ mol^{-1}) would most likely be explained by the difference in experimental conditions of the two studies (Table 2). In reality, the single heating rate method has such a large value of $\Delta E_{\mathrm{method}}$ (72.2 to 156.7 kJ mol^{-1}) that comparison with other values is not practically feasible.

Conclusions

The differences in the values of the activation energy determined for the same solid state process are commonly ascribed to the differences in experimental conditions and sample characteristics. Although these fluctuations in the process are an important source of uncertainty in the experimental value of the activation energy ($\Delta E_{\mathrm{process}}$), one should not forget that there also is an uncertainty associated with the method of computation of the activation energy ($\Delta E_{\mathrm{method}}$). This uncertainty differs markedly for single and multiple heating rate methods. A method that uses fitting of single heating rate data to various reaction models is shown to yield highly uncertain values of the activation energy. The resulting value of $\Delta E_{\mathrm{method}}$ appears to be large enough to explain significant differences in the activation energies reported by different workers. It is our feeling that quite often the observed differences in the activation energy are mistakenly ascribed to $\Delta E_{\mathrm{process}}$, when they should be ascribed to the large uncertainty associated with the use of a single heating rate method. Because of this uncertainty, the activation energies obtained by these methods are rather unlikely to reliably detect the changes in experimental conditions and sample characteristics. Generally, we recommend to avoid using the activation energies estimated by these methods as reference values for comparison purposes.

A multiple heating rate isoconversional method is demonstrated to significantly reduce the value of $\Delta E_{\mathrm{method}}$. For this reason, the activation energies determined by such methods provide reliable reference values. Also, these activation energies are likely to be capable of reflecting the changes in experimental conditions and sample characteristics, subject to $\Delta E_{\mathrm{process}} > \Delta E_{\mathrm{method}}$.

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