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ON THE ACCURACY AND PRECISION OF ESTIMATION OF THE ACTIVATION ENERGY OF NON-ISOTHERMAL DECOMPOSITION OF A SOLID

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The agreement between the estimates and an independently calculated value of the activation energy, and the least squares criterion, have been used as alternative criteria for discriminating between rivalling kinetic models of the non-isothermal decomposition of a solid. It is shown that the two criteria are in good agreement when the data embrace a wide range of thermal curves with different heating rates.

The conditions are discussed for determination of the most accurate and precise estimates of the activation energy and the other model parameters by the non-linear estimation approach.

The discussion is supported by calculations performed on experimental results of dehydration of $CaC_2O_4 \cdot H_2O$ and $Ba(IO_3)_2 \cdot H_2O$.

Determination of the activation energy and other kinetic parameters of thermal decomposition of solids from thermogravimetric experiments can be defined as a problem of model identification. Different methods of identification used by various authors [1, 2] require specific types of data, collected under special experimental conditions, e.g. differential or integral data from isothermal runs or from runs conducted at constant heating rate. As a rule, individual methods are valid only for selected forms of kinetic models.

The development of various methods for identification of decomposition models stemmed from a desire to simplify laborious procedures for mathematical processing of experimental results. However, in the elaboration of these methods some assumptions were made that are difficult to fulfil in real experiments, e.g. linear temperature rise.

Nowadays the advance in numerical, computer-oriented methods, such as the non-linear least squares, maximum likelihood, quasi-linearization and others [3—5], allows one to overcome the computational problems of identification. Effective optimization procedures are capable of handling models of any complexity. The problem is how to choose from among the various possible models the one that would be applicable over the widest range of experimental conditions.

The criteria for the planning of experiments have also undergone some changes. Instead of the experiments being planned to make the measurement data fulfil the assumptions of a simplified method for data treatment, the experiments are now designed to provide the maximum volume of information on individual parameters. It is important that studies be carried out under experimental conditions that allow one to determine the most accurate, precise and least correlated estimates of model parameters.

Here, we use a method for estimating the activation energy from non-isothermal data without considering the form of the kinetic model. The activation energy found in this way is subsequently used as a reference value for discriminating between various thermal decomposition models. Having such a reference value and a selected approximate kinetic model, we then discuss how the range of experimental data and the accuracy of the model affect the estimates of the activation energy calculated by non-linear estimation.

Theoretical analysis

For the thermal dissociation of a solid, represented by the equation

$$A_s \rightarrow B_s + C_g \tag{1}$$

the degree of conversion may be defined by the formula

$$\alpha = m_c/m_{c\infty} \tag{2}$$

where m_c = mass loss of the sample at time t (mass of the gaseous product C released), and $m_{c\infty}$ = total mass loss of the sample during decomposition.

In the general form, the rate of thermal decomposition may be represented by the kinetic model

$$\dot{\alpha} = k_0 \exp(-E/RT) f(\alpha) \tag{3}$$

in which k_0 = pre-exponential factor, E = activation energy, R = gas constant, $f(\alpha)$ = function depending on reaction mechanism, and $\dot{\alpha} = \mathrm{d}\alpha/\mathrm{d}t$ = decomposition rate.

The value of the activation energy in Eq. (3) can be estimated simply from the differential (i.e. reaction rate *vs.* time) data by non-linear least squares method. Similar methods, but involving intergration of the rate squation, can be used to determine the activation energy from integral (i.e. conversion *vs.* time) data [4]. In both cases, to estimate the activation energy it is necessary to assume a functional form $f(\alpha)$ for the reaction mechanism, which is an additional source of error in estimation.

However, by performing the experiments at several heating rates and by proper grouping of the data it is possible to separate the information on activation energy from that on $f(\alpha)$, and consequently to estimate the activation energy without considering the form of function $f(\alpha)$. The idea was presented by Anderson [6] and by Friedman [7], and was recently discussed by Merzhanov *et al.* in a survey [8]

For experimental data that are grouped with respect to the values α_j of the conversion degree, taken from thermal curves recorded at different heating rates, Eq. (3) assumes the following form

$$\dot{\alpha}_{ij} = k_0 \exp(-E_j/RT_{ij}) f(\alpha_j) \tag{4}$$

where subscript $i = 1, 2, \ldots$ denotes the sequential experimental runs, i.e. the sequential thermal curve subscript $j = 1, 2, \ldots$ denotes the reading of $\dot{\alpha}$ and T at a time when $\alpha = \alpha_j$, and E_j = activation energy at the conversion degree α_j.

For a fixed j, i.e. for a fixed conversion degree α_j = const., Eq. (4) may be rewritten as

$$\dot{\alpha}_i = \exp\left(-E/RT_i\right) c \tag{5}$$

where c = const.

The fixed subscript j is dropped from the terms $\dot{\alpha}_i$, T_i and E to make the notation more clear, but it is understood that the equation holds for the data selected according to the given value of the conversion degree.

Provided the data are collected from several runs performed at different heating rates, the activation energy may be estimated from Eq. (5) for any given conversion degree, without considering the reaction mechanism and its functional form $f(\alpha)$. If the activation energy does not depend, within the limits of estimation error, on the value of the conversion degree, the estimation can be carried out on all the experimental data simultaneously, according to the equation

$$\dot{\alpha}_{ij} = \exp\left(-E/RT_{ij}\right) c_j \tag{6}$$

in which $c_j = k_0 f(\alpha_j)$.

The initial guesses of activation energy for an iterative, non-linear regression procedure can be found by the linear least squares method from Eqs (7) and (8), which are the logarithmic versions of Eqs (5) and (6), linear with respect to the estimated activation energy

$$\ln\left(\dot{\alpha}_i\right) = -E/RT_i + \ln c \tag{7}$$

$$\ln\left(\dot{\alpha}_{ij}\right) = -E/RT_{ij} + \ln c_j\,. \tag{8}$$

If a theoretically based functional form for $f(\alpha)$ is known, the activation energy together with the function parameters can be estimated directly from Eq. (3). In that case, it is not necessary to group the experimental data. However, the precision of the estimation depends on the adequacy of the function $f(\alpha)$, and the estimates of the activation energy are correlated with the estimates of the function parameters. Unless the data embrace a very wide range of different heating rates, a poorly-assumed reaction mechanism may cause a serious error in the estimate of the activation energy. Estimating the activation energy on the basis of one experimental run is justified only when the adequacy of the assumed reaction mechanism under given experimental conditions is unquestionable.

Experimental

In experiments, the mass loss of the sample and temperature were recorded in the thermal curves TG and T, respectively. By reading the values of TG and T at given time intervals, the set of data $m_c(t)$ and $T(t)$ was assembled. From these data, the values of the conversion degree as a function of time $\alpha(t)$ were calculated using Eq. (2). Finally, the rates $\dot{\alpha}(t)$ were obtained by numerical differentiation and smoothing of the data $\alpha(t)$.

The set of data $\alpha(t)$, $\dot{\alpha}(t)$ and $T(t)$ read at arbitrarily chosen moments t_j ($j = 1, 2, \ldots$) is a basic set for the estimation of the activation energy. However, if the activation energy is to be estimated without assuming the functional form of $f(\alpha)$, several sets of data are needed with identical values of the conversion degree at corresponding points, i.e.

$$\alpha(t_{ij}) = \alpha(t_{kj}) \quad \text{or} \quad \alpha_{ij} = \alpha_{kj} = \alpha_j \tag{9}$$

where subscripts i, k denote different thermal curves and subscript j denotes a sequential measurement point.

These data are easily assembled by reading or interpolating the measurements at the moments, different for different experimental runs, corresponding to given values of the conversion degree.

An example of the data converted according to the described procedure is given in Table 1. For the nine values of the conversion degree α_j($j = 1, \ldots, 9$) listed in column 1, the respective values of temperature T_{ij} and decomposition rate $\dot{\alpha}_{ij}$ ($i = 1, 2, 3$) were read off three curves recorded at three different heating rates (see next section). The measurement times are not listed in the Table because they are not essential to the proposed method.

Dehydration of $CaC_2O_4 \cdot H_2O$. Estimation of the average activation energy value

The activation energy of $CaC_2O_4 \cdot H_2O$ dehydration was estimated from three thermal curves recorded at three heating rates (2.3, 7.4 and 14.8°/min) on a MOM Paulik–Paulik–Erdey derivatograph. The samples, with initial mass 270 mg, were heated in a standard platinum crucible under a static air atmosphere.

The estimation was carried out by weighted non-linear regression according to Eq. (6), with the measurement points given statistical weights inversely proportional to the respective values of $\dot{\alpha}_{ij}$.

The estimated value of the activation energy, 97.3 ± 7.5* kJ/mole (23.25 kcal/mole), compares well with the values reported by other authors, e.g. [9].

The dehydration rates calculated from Eq. (6) are in good agreement with the experimental data (Table 1).

a. Estimation of the activation energy as a function of the conversion degree

The activation energy of $Ba(IO_3)_2 \cdot H_2O$ dehydration was estimated from measurements in 8 experiments carried out at several different heating rates (Table 4). The pairs of curves 3 and 4, and 5 and 6, are repeated runs that correspond to

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* All confidence intervals in this paper are given at the probability level of 0.95.

Table 1

Example of experimental data and comparison of experimental $CaC_2O_4 \cdot H_2O$ dehydration rates with those calculated from Eq. (6)

α	T	$\dot{\alpha}_{\text{exptl.}}$	$\dot{\alpha}_{\text{calc.}}$
	K	$\times 10^{-3} \text{min}^{-1}$	$\times 10^{-3} \text{min}^{-1}$
0.1	426	10	12
	446	36	41
	450.5	63	53
0.2	440	22	21
	461.5	68	74
	467	107	100
0.3	449	31	28
	471.5	90	98
	478	145	138
0.4	455	38	33
	479.5	110	122
	486	178	169
0.5	460.5	45	38
	485.5	131	142
	493	211	205
0.6	465.5	50	43
	491.5	151	164
	499.5	247	239
0.7	471	53	50
	496.5	166	178
	505	275	264
0.8	475	54	52
	501	173	187
	509.5	289	276
0.9	479.5	52	50
	507	164	183
	514.5	283	262

identical experimental conditions. The differences in the average heating rates and in the conversion rates could be attributed to some uncontrolled random disturbances that normally occur during experiments.

The dehydration rate expressed by Eq. (7) was fitted by the linear least squares method to the experimental values of $\dot{\alpha}_{ij}$ at the respective temperatures T_{ij} for 11 values of the conversion degree separately. Table 2 shows the results of the estimation and the precision of fit represented by the linear correlation coefficient R.

The values of the activation energy, as listed in Table 2, were next used in Eq. (5) to calculate the dehydration rate. From the differences between the experimental and calculated values of the dehydration rate, the variance s^2 of dehydration rate measurements was estimated over the whole range of $\dot{\alpha}$ values and approximated by a formula

$$s^2 = 0.01\,\dot{\alpha}^2 \tag{10}$$

The variance given by Eq. (10) was used to calculate statistical weights w for the experimental points, according to the formula

$$w = k/s^2 \tag{11}$$

where k = proportionality factor.

From the weighted experimental data, the adjusted estimates of the activation energy and their respective confidence intervals were determined according to Eq. (5). Since Eq. (5) is non-linear with respect to the activation energy, the weighted non-linear regression technique described in [4] was used to find the optimum activation energy estimates.

The confidence intervals and the linear correlation coefficients in Table 2 indicate that for the conversion degrees 0.05 and 0.1 the experimental data are widely scattered. Therefore, further calculations were restricted to the conversion range 0.2–0.95.

The estimation of the average activation energy over the chosen range of α was performed by the weighted non-linear regression procedure according to Eq. (6). As shown in Fig. 1, the values of the activation energy for the individual

Table 2

Activation energy of $Ba(IO_3)_2 \cdot H_2O$ dehydration for succesive values of conversion degree

Conversion α	Activation energy E^1	Activation energy E^2	Confidence interval $\pm \Delta E$	Linear correlation coefficient R
	linear regression	nonlinear regression		
—	kJ/mole	kJ/mole	kJ/mole	
0.05	90.9	92.1	63.6	0.82
0.1	81.6	83.7	56.1	0.85
0.2	72.4	71.6	36.4	0.91
0.3	73.3	72.4	22.6	0.96
0.4	69.1	67.4	18.4	0.97
0.5	67.0	66.2	18.8	0.96
0.6	68.2	66.6	15.5	0.98
0.7	71.2	70.8	13.8	0.98
0.8	71.6	69.5	13.8	0.99
0.9	73.3	70.3	14.2	0.98
0.95	71.2	70.8	17.6	0.98
0.2–0.95	—	68.2[3]	4.6	—

[1] according to Eq. (7)
[2] according to Eq. (5)
[3] according to Eq. (6)

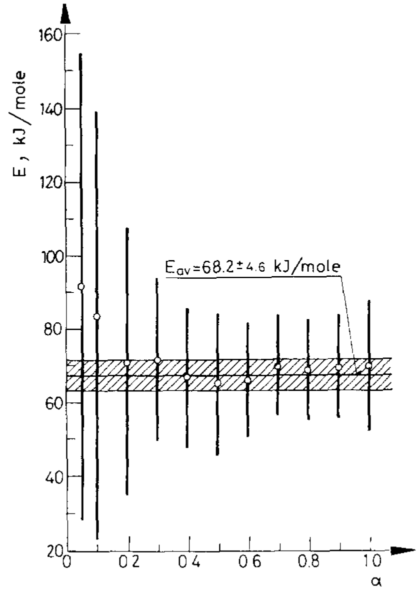

Fig. 1. Activation energy of $Ba(IO_3)_2 \cdot H_2O$ dehydration as a function of conversion degree. Vertical bars denote 95% confidence intervals

degrees of conversion are within the confidence interval for the average activation energy. Therefore, the activation energy of $Ba(IO_3)_2 \cdot H_2O$ dehydration can be considered constant, 68.2 ± 4.6 kJ/mole (16.3 kcal/mole).

b. Kinetic model

The same experimental data as in the previous section were used to determine the form of the function $f(\alpha)$ and to estimate the function parameters. It is worth noting however, that grouping of the data was not essential to these calculations.

The estimation of parameters was carried out using Eq. (3), with various versions of the function $f(\alpha)$, corresponding to different tentative kinetic models. The initial guesses of the parameters for the iterative weighted non-linear regression were calculated by the linear least squares method applied to the logarithmic form of Eq. (3), which is linear with respect to the parameters.

Two measures were used to discriminate between various kinetic models: the least squares criterion, i.e. the weighted sum of squared deviations from the experimental dehydration rates, and the agreement of the activation energy in the model with the value 68.2. kJ/mole found independently of the functional from of $f(\alpha)$.

Since the experimental data were designed to separate the information on activation energy from that on $f(\alpha)$, the two criteria were in good agreement;

it can be shown, however, that for a single experimental run, a complex model may best fit the data while having an unreasonable activation energy value [4].

The best fit of the experimental data was achieved, as expected, with the purely empirical, five-parameter model (Table 3), but a good approximation of the $Ba(IO_3)_2 \cdot H_2O$ dehydration rate was also obtained with a simple, three-parameter model

$$\dot{\alpha} = \exp(-65.3/RT + 19.3)(1 - \alpha)^{3/4} \qquad (12)$$

where the activation energy is expressed in kJ/mole.

The value of the activation energy in Eq. (12) lies within the confidence limits for the independently determined activation energy.

In order to assess the effect of the experimental data range on the precision of estimation, the activation energy and the other kinetic parameters of Eq. (12) were estimated by the weighted non-linear least squares method from the individual experimental runs. The results, summarized in Table 4, show that the differences between the estimates are significant even for the runs corresponding to similar experimental conditions.

It is worth noting that the estimate of the activation energy computed as an average from the eight individual curves is significantly lower then the value estimated from all the curves simultaneously. The same is true for the other kinetic parameters. The result has to be attributed to a high correlation between the model parameter estimates calculated from the individual thermal curves. This correlation is reasonably reduced when the estimation is based on all the data used simultaneously.

In the next calculations (Table 5), in which the function exponent was fixed, the discrepancies between the values of the activation energy estimated from the

Table 3

Parameters of the kinetic model of $Ba(IO_3)_2 \cdot H_2O$ dehydration estimated by weighted nonlinear least squares for various forms of function $f(\alpha)$ in Eq. (3)

$f(\alpha)$	E, kJ/mole	$\ln k_0$	m	n	p	Weighted sum of squares criterion
$(1-\alpha)^{2/3}$	61.1	17.8				94.2
$(1-\alpha)^m$	65.3	19.3	0.75			84.2
$(-\ln(1-\alpha))^p$	70.3	19.8			0.90	237.8
$(1-\alpha)^m\alpha^n$	67.8	20.0	0.69	−0.22		76.0
$(1-\alpha)^m(-\ln(1-\alpha))^p$	67.8	20.0	0.63		−0.19	76.7
$\alpha^n(-\ln(1-\alpha))^p$	67.8	20.2		2.0	−2.04	84.7
$(1-\alpha)^m\alpha^n(-\ln(1-\alpha))^p$	68.2	19.4	1.90	−4.17	3.62	70.1
$(1-\alpha)^{1/3}/(1-(1-\alpha)^{1/3})$	86.2	24.1				217.1
$(1-\alpha)^{2/3}/(1-(1-\alpha)^{1/3})$	104.7	30.3				348.2

Table 4

Activation energy of $Ba(IO_3)_2 \cdot H_2O$ dehydration estimated from individual thermograms using model

$$\dot{\alpha} = k_0 \exp(-E/RT)(1-\alpha)^m$$

I. Simultaneous estimation of E, $\ln k_0$ and m

Thermal curve No.	Average heating rate	E	s_E/E	$\ln k_0$	$\frac{s_{\ln k_0}}{\ln k_0}$	m	s_m/m	$\rho_{E,m}$	Sum of squares
	°/min	kJ/mole	—	—	—	—	—	—	—
1	1.35	62.8	0.36	18.2	0.42	0.72	0.33	0.92	0.27
2	2.35	57.4	0.26	16.7	0.30	0.75	0.24	0.92	0.08
3	3.00	51.1	0.24	14.7	0.28	0.63	0.24	0.92	1.29
4	3.90	57.4	0.19	16.5	0.22	0.54	0.22	0.90	0.63
5	6.30	56.1	0.15	16.5	0.17	0.68	0.16	0.91	0.62
6	6.43	56.5	0.15	16.2	0.17	0.64	0.16	0.90	1.59
7	8.20	57.8	0.13	17.0	0.15	0.69	0.15	0.90	5.24
8	8.83	47.7	0.16	13.7	0.18	0.61	0.17	0.91	2.07
Average	—	55.9	—	16.2	—	0.66	—	—	1.47
1–8[1]	—	65.3	0.03	19.3	0.03	0.75	0.04	0.75	84.2

s — estimate of standard deviation

s_E/E — relative standard deviation (variation coefficient)

$\rho_{E,m}$ — coefficient of correlation between E and m estimates

[1] Estimation based on all the curves simultaneously

Table 5

Activation energy of $Ba(IO_3)_2 \cdot H_2O$ dehydration estimated from individual curves using model

$$\dot{\alpha} = k_0 \exp(-E/RT)(1-\alpha)^m$$

II. Estimation of activation energy with other parameters fixed

Thermal curve No.	$m = 0.75$					$m = 0.75$, $\ln k_0 = 19.3$		
	E	s_E/E	$\ln k_0$	$\frac{s_{\ln k_0}}{\ln k_0}$	Sum of squares	E	s_E/E	Sum of squares
	kJ/mole	—	—	—	—	kJ mole	—	—
1	65.7	0.13	19.2	0.15	0.30	65.7	0.032	0.30
2	57.8	0.10	16.9	0.11	0.08	65.3	0.025	1.69
3	60.3	0.08	17.8	0.09	1.92	64.9	0.023	2.68
4	74.5	0.07	22.2	0.07	3.60	65.3	0.021	6.78
5	61.5	0.06	18.3	0.06	1.06	64.5	0.019	1.75
6	64.1	0.06	18.8	0.06	2.65	65.3	0.019	2.78
7	62.8	0.05	18.6	0.06	5.70	64.9	0.018	6.08
8	57.8	0.06	17.0	0.06	4.06	65.3	0.018	8.31
Average	63.1	—	18.6	—	2.42	65.2	—	3.80

different curves were much lower. The average value of the activation energy was also close to the value based on the simultaneous estimation.

Finally, calculations were made (Table 5) in which only the activation energy was estimated and the other parameters were fixed. In this case, the values of the activation energy determined from different experimental runs were within the range 64.5 – 65.7 kJ/mole.

In all calculations performed, the precision of the estimates (expressed by relative standard deviations) was better for thermal curves with higher heating rates. The minor expections from this rule for curves 7 and 8 are a result of non-linearities in the heating programs.

Conclusions

By grouping the experimental data according to the values of the conversion degree it is possible to estimate the activation energy as a function of the conversion degree, or the average value of the activation energy, without assuming the form of the kinetic model. Such an independently estimated, average value of the activation energy may be used as a reference value for discriminating between different kinetic models of thermal decomposition.

The precision and accuracy of estimation of model parameters depend on the range of the experimental data and on the accuracy of the assumed model. As a rule, a series of experiments at several heating rates is needed to determine precisely the activation energy and the form of the kinetic model together with its parameters.

When a sufficiently broad range of experimental data taken at different heating rates is used in calculations, the least squares criterion is sufficient to discriminate between rivalling kinetic models. The better the fit to the experimental data, the more accurate the estimates of the activation energy.

This is not true, however, when a single curve is taken for calculations. The more parameters to be estimated in an approximate model, the more they are influenced by random disturbances in the experiment, and the less reliable are the estimates. An estimation based on averaging the estimates from individual curves can lead to wrong results.

The data from a single non-isothermal run can be properly used to estimate the activation energy only when definite *a priori* knowledge is available about the reaction mechanism, perhaps from theoretical consideration or from previous studies of the process. The precision of estimates is better for thermal curves with higher heating rates.

The most accurate and precise results can be obtained by using a non-linear estimation approach based on an adequate kinetic model and on all the curves simultaneously.

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Résumé — On s'est servi d'une énergie d'activation estimée indépendamment et du critère des moindres carrés pour choisir parmi les différents modèles cinétiques proposés pour la décomposition non-isotherme d'un corps solide. On a montré que les deux critères sont en bon accord, pourvu que les données portent sur un grand nombre de courbes TG obtenues avec différentes vitesses de chauffage.

On discute les conditions nécessaires pour déterminer de manière exacte et précise l'énergie d'activation et les autres paramètres modèles en utilisant la méthode par approximations non linéaires.

Des calculs effectués sur des résultats d'expériences obtenus dans le cas de la déshydratation de $CaC_2O_4 \cdot H_2O$ et de $Ba(IO_3)_2 \cdot H_2O$ viennent à l'appui de la discussion.

Zusammenfassung — Die Übereinstimmung zwischen der geschätzten und einer unabhängig kalkulierten Aktivierungsenergie sowie das Kriterium der kleinsten Quadrate wurden als alternative Kriterien zur Unterscheidung zwischen konkurrierenden kinetischen Modellen der nicht-isothermen Zersetzung eines Festkörpers herangezogen. Es wurde gezeigt, daß die beiden Kriterien gut übereinstimmen, wenn sich die Daten auf ein weites Gebiet von Thermogrammen verschiedener Aufheizgeschwindigkeit erstrecken.

Die Bedingungen zur Bestimmung äußerst genauer und präziser Schätzwerte der Aktivierungsenergie und der anderen Modellparameter durch nichtlineare Schätzungsnäherung wurden erörtert.

Diese Erörterungen wurden durch Berechnungen aus Versuchsergebnissen der Dehydratisierung von $CaC_2O_4 \cdot H_2O$ und $Ba(IO_3)_2 \cdot H_2O$ bestätigt.

Резюме — Согласие между оценочными и независимо вычисленным значением энергии активации, а также метод наименьших квадратов были использованы как альтернативный критерий для различия конкурентных кинетических моделей неизотермического разложения твердых тел. Показано, что эти два критерия хорошо согласуются, когда данные содержат широкую область термограмм с различными скоростями нагрева. Обсуждены условия определения наиболее точных и совершенных оценок энергии активации и других модельных параметров с помощью нелинейного оценочного приближения. Обсуждение было подтвердено вычислениями, проведенными с экспериментальными результатами дегидратации $CaC_2O_4 \cdot H_2O$ и $Ba(IO_3)_2 . H_2O$.