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Determination of kinetic parameters by direct non-linear regression from TG curves

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Abstract

A method of direct non-linear regression of the kinetic equation was proposed for a simultaneous calculation of the activation energy, frequency factor, and reaction order from a single TG curve. The method of calculation was utilized for the kinetic parameters calculation from both the simulated and experimental curves (graphite and soot oxidation, $Mg(OH)_2$ decomposition). The results were compared with the values obtained by traditional methods. A dependence of the calculated parameters on random errors of the experimental data was studied. The method of non-linear regression appears to be the best of the used methods from this point of view. It was proved that the proposed calculation method is as well applicable for the kinetic parameters calculation of more overlapping processes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Thermogravimetry; Non-linear regression; Overlapping processes

1. Introduction

The non-isothermal thermogravimetry (TG) with a linear temperature growth is a method frequently used to characterize materials from their thermal behavior standpoint. In addition, it enables to determine apparent kinetic parameters of heterogeneous reactions (the reaction order *n*, the activation energy *E*, and the frequency factor *A*).

Considerable attention is paid to the kinetic parameters calculation from TG curves. New calculation methods are still being published [1–7]. A number of papers are devoted to comparing these methods [7–9] or to their critical assessment [10,11].

The present calculation methods are either based on a single TG curve (‘‘single curve’’ methods) or require several TG curves measured at various heating rates (‘‘many curves’’ methods, isoconversion methods).

Though, a physical meaning of the kinetic parameters determined by ‘‘single curve’’ methods is not quite clear, these methods are able to describe a TG curve generally well. Moreover, the dependence of the calculated kinetic parameters on experimental conditions may bring new knowledge about the corresponding thermal process.

The ‘‘single curve’’ methods are based on a linearization of the fundamental kinetic equation. They are relatively satisfactory for simple processes where their results are well comparable. However, if a TG curve consists of two or more overlapping processes, the ‘‘single curve’’ methods usually fail. The reason of the failure is the kinetic equation linearization which may be performed in the curve section where only a single process proceeds.

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Recent expansion and development of computers make the iterative methods utilizing the direct non-linear evaluation of TG curves possible. Paper [12] showed a utilizability of the non-linear regression as a method of determining the kinetic parameters of heterogeneous reactions from TG curves, which supports the justifiability of this approach.

The present paper aims to prove possibilities of determining all the kinetic parameters by means of the direct non-linear regression (DNR) of the basic kinetic equation and to propose a method of their calculation from a single TG curve. Another aim is to verify the assumption that the elimination of the kinetic equation linearization maintains its additive feature and enables to calculate the kinetic parameters for several overlapping processes.

2. Theoretical

Kinetic calculations from the thermogravimetric data usually proceed from the basic kinetic equation

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = k(T)g(m) \tag{1}$$

where m is the actual substance mass, t the time, and T the absolute temperature.

Arrhenius equation is generally used for the dependence of the rate constant $k(T)$ on the absolute temperature

$$k(T) = A\,\mathrm{e}^{-E_p/RT} \tag{2}$$

where A is the frequency factor, E_p the activation energy, and R the molar gas constant.

The mass function $g(m)$ is dependent on the assumed reaction mechanism. Various forms of this function have been published [13]. We used the form analogous to the homogeneous reactions kinetics in our calculations

$$g(m) = m^n \tag{3}$$

where n is the reaction order.

This form is often applied for calculations of the kinetic parameters of heterogeneous thermal processes. It was used for solving, e.g. the oxidation kinetics of rocket fuels [14], coal [8,15], char [16], graphite [15,17,18], and/or diamond [18].

Inserting Eqs. (2) and (3) in Eq. (1), we obtain the kinetic equation in the following form:

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = A\,\mathrm{e}^{-E_p/RT}\,m^n \tag{4}$$

To calculate a theoretical TG curve, it is necessary to know the form of the function $m = f(t, E, A, n)$. If the time step is set small enough, the derivatives in Eq. (4) may be replaced by differences. We assume that the TG curve is composed of very small linear segments of the length Δt, in which the reaction rate is constant.

$$\Delta m = -A\,\mathrm{e}^{-E_p/RT}\,m^n\,\Delta t \tag{5}$$

Assuming the reacting substance mass m_0 and temperature T_0 at the beginning of the TG curve (time $t_0 = 0$), further points of the curve can be calculated from the following recurrence relation:

$$m_i = m_{i-1} - A\,\mathrm{e}^{-E_p/RT_{i-1}}\,m_{i-1}^n(t_i - t_{i-1}) \tag{6}$$

Eq. (6) is additive for several parallel processes. It can be expanded for p various processes.

$$m_i = \sum_p m_{p,i-1} - \sum_p A_p\,\mathrm{e}^{-E_p/RT_{i-1}}\,m_{p,i-1}^{n_p}(t_i - t_{i-1}) \tag{7}$$

2.1. Direct non-linear regression

The calculation of kinetic parameters from Eq. (7) seems to be a simple problem. We have an experimental curve and the equation enabling to calculate a theoretical curve for the given E, A, and n parameters. Searching for these parameters is a typical regression problem. Eq. (7) is non-linear in relation to the searched parameters. Therefore, it is necessary to apply non-linear regression methods.

There are numerous computer programs for non-linear regression calculations. Most of them, however, are not applicable to searching for the kinetic parameters from Eq. (7). One of the reasons is the fact that commonly available software requires a regression function in an analytic form and does not allow to use a recurrent relation. In addition, common optimization methods applied in non-linear regression fail with Eq. (7).

Non-linear regression is based on repeating two basic steps.

1. Setting parameters values.
2. Evaluation of the set parameters values.

In the course of repeating these steps, the best values of the parameters are stored and they are presented as results after finishing the calculation.

There are a number of algorithms (optimization methods) for setting parameters values enabling to find the best values fast. To evaluate the set parameters, the residual sum of squares of deviations of experimental and calculated regression function values (RSS) is commonly used. It is defined for Eq. (7) by the following relation:

$$\mathrm{RSS} = \sum_{i=1}^{p} (m_{\mathrm{c}_i} - m_{\mathrm{e}_i})^2 \tag{8}$$

where m_{e_i} are the specimen masses in individual points of the experimental curve and m_{c_i} the values calculated from Eq. (7) in the corresponding points. The least RSS values are obtained for the best parameter estimates.

The results obtained by means of current optimization methods utilizing RSS optimization criterion are not good. The calculation converges badly to correct values and final results depend on initial estimates of the kinetic parameters. These problems are encountered even in calculations from purely theoretical curves not burdened with experimental noise.

The following procedure (Section 2.2) was proposed after the optimization procedure analysis.

2.2. Kinetic parameters searching — step by step

The kinetic parameters E, A, and n are not generally the only unknown parameters in Eq. (7). For its utilization, it is necessary to know initial masses of reacting substances for each particular process. In some cases (if the specimen composition is known), these masses are known, or they also have to be searched for by means of regression calculations.

For p processes, we have to search for the set of parameters E_j, A_j, n_j ($j = 1, 2, \ldots, p$) and mass fractions $w_{0,j}$ ($j = 1, 2, \ldots, p-1$) that determine the portion of individual reacting components.

The fundamentals of the presented method of calculation of kinetic parameters are as follows.

1. The kinetic energies E_j and reaction orders n_j are searched by gradual searching through the opted range of values with the set accuracy.
2. The frequency factors A_j and mass fractions w_j are searched separately for each combination of the E_j and n_j values.
3. The reciprocal value of the residual sum of squares 1/RSS is used as a criterion for the quality assessment of the parameters. It reaches its maximum for the best parameters.

The basic algorithm of the calculation is shown in Fig. 1. At the beginning, a range and step for the activation energy and reaction order searching have to be opted. The option of these values depend on the information available about the processes in question and on the required calculation accuracy. The wider the interval for searching and the less the steps are, the longer the time of calculation is. It was proved convenient in our calculations to start with a wide interval and a relatively high step (e.g. $\min E = 20$, $\max E = 300$, $\mathrm{step}\,E = 10$, $\min n = 0$, $\max n = 2$, $\mathrm{step}\,n = 0.2$). Then more precise results may be obtained by repeating the whole calculation procedure with a narrower interval and smaller step for the E_j and n_j searching.

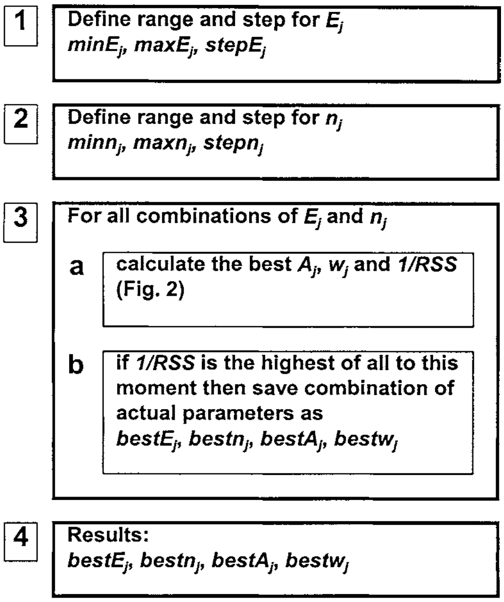
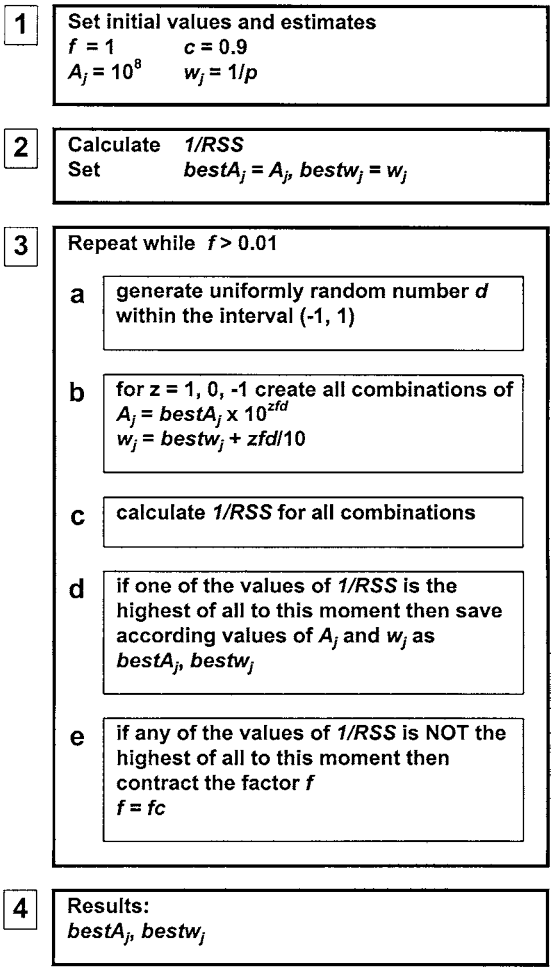


Fig. 1. Scheme of the basic algorithm.



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1  Set initial values and estimates
     $f = 1$        $c = 0.9$
     $A_j = 10^8$   $w_j = 1/p$

2  Calculate  $1/RSS$
   Set        $bestA_j = A_j$, $bestw_j = w_j$

3  Repeat while $f > 0.01$
     a  generate uniformly random number $d$
        within the interval (-1, 1)
     b  for z = 1, 0, -1 create all combinations of
          $A_j = bestA_j \times 10^{zfd}$
          $w_j = bestw_j + zfd/10$
     c  calculate $1/RSS$ for all combinations
     d  if one of the values of $1/RSS$ is the
        highest of all to this moment then save
        according values of $A_j$ and $w_j$ as
        $bestA_j$, $bestw_j$
     e  if any of the values of $1/RSS$ is NOT the
        highest of all to this moment then
        contract the factor $f$
          $f = fc$

4  Results:
   $bestA_j$, $bestw_j$
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Fig. 2. Algorithm of A_j and w_j calculation.

The frequency factors and mass fractions for individual combinations of E_j and n_j may be calculated by means of the algorithm shown in Fig. 2. The procedure is based on the commonly used method with a random increment.

3. Experimental

The thermogravimetric experiments were performed on the apparatus Netzsch STA 409 EP under same experimental conditions: Al_2O_3 crucibles, without a standard, the heating rate $10\,K\,min^{-1}$, the dynamic atmosphere (dry air, $100\,cm^3\,min^{-1}$), the sample mass 4.9–5.1 mg.

The used materials were graphite (Fluka, grain size <0.1 mm) and soot Vulcan 3 (Cabot, fraction under 0.1 mm).

The published thermogravimetric data for the thermal dehydroxylation of $Mg(OH)_2$ [19] were used for testing.

The integral methods by Coats and Redfern (CR) [20], Horowitz and Metzger (HM) [21], and differential methods by Freeman and Carroll (FC) [22], Vachuska and Voboril (VV) [23] were used for comparative calculations. The parts of the curves corresponding to the range of conversion 0.05–0.95 were taken for calculations. The reaction orders in integral methods were determined by the method of trials and errors. The calculated order corresponds to the best linear dependence calculated applying the least squares method. The calculated values of the activation energy were rounded off to 1 kJ mol^{-1}, the values of the frequency factor and reaction order were rounded off to two valid digits.

In the calculations applying the described method of the direct non-linear regression, the whole TG curves were taken and the least used difference was 1 kJ mol^{-1} for the activation energy and 0.1 for the reaction order. The optimized frequency factor was rounded off to two valid digits likewise in the comparative methods.

4. Results and discussion

4.1. Comparison with other methods

A comparison of the described calculation method with other methods was done on the experimental curves measured in our laboratory (oxidation of graphite and soot), on the published data for the thermal decomposition of magnesium hydroxide [19], and on the curves generated according to Eq. (6) with various parameters. The results of calculations are summarized in Table 1.

The calculated kinetic parameters show a considerable accordance nearly for all the methods. The method by Horowitz and Metzger is an exception that gives, in comparison with the other methods, considerably higher values of E and A, and in some cases unreliable values of n. However, this fact is known [7].

Table 1
The values of E (kJ mol^{-1}), A (s^{-1}), and n calculated by means of various methods[a]

Data	Parameters	DNR	CR	HM	FC	VV
1	E	206	201	241	207	210
	A	1.9×10^8	1.3×10^7	1.0×10^9	–	–
	n	0.6	0.4	0.4	0.5	0.5
2	E	206	215	281	209	215
	A	4.0×10^9	1.2×10^{10}	1.2×10^{14}	–	–
	n	0.9	0.9	1.5	0.9	1.0
3	E	212	214	233	211	200
	A	1.5×10^{14}	5.2×10^{14}	1.5×10^{16}	–	–
	n	1.6	1.4	1.0	1.3	1.3
4	E	161	163	192	164	163
	A	1.2×10^8	8.3×10^7	6.3×10^9	–	–
	n	0.6	0.6	0.6	0.6	0.6
5	E	160	160	193	163	163
	A	1.0×10^8	5.6×10^7	7.4×10^9	–	–
	n	0.6	0.6	0.7	0.6	0.6
6	E	86	88	109	88	89
	A	4.4×10^4	9.5×10^4	5.1×10^6	–	–
	n	1.2	1.2	1.3	1.2	1.2
7	E	86	86	112	87	88
	A	4.4×10^4	5.9×10^4	1.2×10^7	–	–
	n	1.2	1.2	1.5	1.2	1.2

[a] Data: 1: graphite oxidation; 2: Vulcan 3 oxidation; 3: $Mg(OH)_2$ decomposition [19] ($E = 223$ kJ mol^{-1}, $A = 1.4 \times 10^{15}$, $n = 1.6$); 4: calculated ($E = 163$ kJ mol^{-1}, $A = 1.6 \times 10^8$ s^{-1}, $n = 0.65$, $\beta = 10$ K min^{-1}, $\Delta t = 30$ s); 5: calculated (same as 4, $\Delta t = 6$ s); 6: calculated ($E = 87$ kJ mol^{-1}, $A = 5.4 \times 10^4$ s^{-1}, $n = 1.23$, $\beta = 10$ K min^{-1}, $\Delta t = 30$ s); 7: calculated (same as 6, $\Delta t = 6$ s).

For data 3 taken from [19] (thermal decomposition of magnesium hydroxide), the method of DNR gives a little higher reaction order than the other methods. But the value $n = 1.6$ is in accordance with the original work. All the methods give for data 3, lower (however, mutually identical) values of the activation energy than the original paper. A probable reason of this fact is a low accuracy of the graphical readings of experimental points in [19].

The couples of the calculated curves 4–5 and 6–7 differ in the used time step Δt, it means in the density of points on the curve. A variation of this parameter had practically no influence on the calculated values for any of the used methods. This fact appears to be quite important for the described method of non-linear regression, since the decrease of the frequency of points enables a considerable acceleration of calculations.

4.2. *Influence of random errors of the mass measuring on the calculated kinetic parameters*

When assessing the influence of random errors of the mass measuring on the calculated parameters, the TG curves burdened by random errors were generated according to Eq. (6). The calculated masses in individual points were adjusted according to the relation

$$m_i(e) = m_i + (2v - 1)\frac{em_i}{100} \tag{15}$$

where $m_i(e)$ is the mass burdened by an error, m_i the original mass calculated according to Eq. (6), e the error expressed in percents of the initial sample mass, and v a uniformly random number from the interval (0, 1).

The curves for $e = 0.1$, 0.5, 1, and 2% were generated. The results of the calculations are summarized in Table 2.

Table 2
The values of E (kJ mol^{-1}), A (s^{-1}), and n calculated by various methods for the data burdened by random errors[a]

Error (%)	Parameters	DNR	CR	HM	FC	VV
±0.1	E	165	166	197	151	161
	A	2.1×10^{8}	1.4×10^{8}	1.2×10^{10}	–	–
	n	0.7	0.6	0.6	0.4	0.6
±0.5	E	164	160	193	129	159
	A	1.8×10^{8}	4.9×10^{7}	6.7×10^{9}	–	–
	n	0.7	0.5	0.6	0.1	0.6
±1	E	164	159	194	215	146
	A	1.8×10^{8}	4.3×10^{7}	8.0×10^{9}	–	–
	n	0.7	0.5	0.6	1.2	0.5
±2	E	173	196	200	313	205
	A	6.4×10^{8}	1.6×10^{10}	2.1×10^{10}	–	–
	n	0.8	1.1	0.6	2.8	0.8

[a] The basic curve: $E = 163$ kJ mol^{-1}; $A = 1.6 \times 10^{8}$ s^{-1}; $n = 0.65$; $\beta = 10$ K min^{-1}; $\Delta t = 30$ s.

The used methods depend on the random error in a different extent. The differential methods (FC, VV) have less stability of solution in relation to the random errors than the integral methods (CF, HM). The worst results give the Freeman and Carrol method, as it was expected. At the error ±0.1%, the calculated values differ considerably from the theoretical ones, and with the increasing error of measurement the results become unreal. The reason of these errors is the fact that the calculation is performed from the difference of two discrete experimental points. The method by Vachuska and Voboril gives a little better results, nevertheless, the difference between the calculated and theoretical values is significant at the errors above 0.5%. The calculation according to Coats and Redfern gives a good accordance at the error as high as 1%. The method by Horowitz and Metzger has excellent stability even at high errors. It can be said, irrespective of a systematic shift of the parameters E and A towards higher values, that this method is nearly independent of the mass measurement errors. The proposed method of DNR may be assessed in a similar way. The values calculated by means of this method are in a very good accordance with the theoretical ones, even at high errors.

4.3. Calculation of two processes

The curves generated according to Eq. (7) and/or their combinations with the experimental curve, were used in calculations of the kinetic parameters for two partly overlapping processes.

Process 1 was only calculated for the parameters $E = 163$ kJ mol^{-1}, $A = 1.6 \times 10^{8}$ s^{-1}, and $n = 0.65$. Process 2 corresponds to the thermal oxidation of soot Vulcan 3 and its parameters were determined above ($E = 206$ kJ mol^{-1}, $A = 4.0 \times 10^{9}$ s^{-1}, $n = 0.9$). The TG curve for this process was either calculated or the experimental data were used. Process 1 was combined with process 2 for various mass proportions of reacting substances. The shape of the combined TG curves with different mass fractions is shown in Fig. 3.

The calculated kinetic parameters for individual curves are summarized in Table 3.

The kinetic parameters determined by a simultaneous calculation applying the direct non-linear

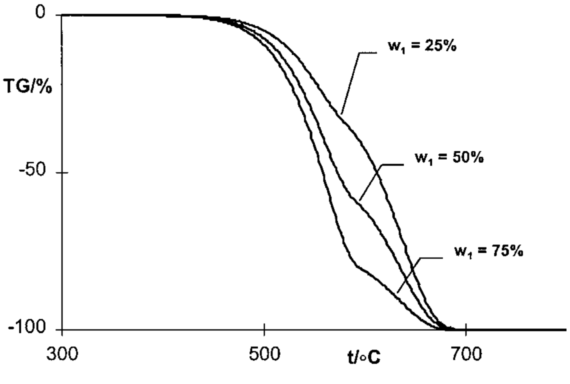

Fig. 3. The TG curves for a couple of overlapping processes.

Table 3
The calculated values of E (kJ mol^{-1}), A (s^{-1}), n, and mass fractions w (%) for the two processes

Data	Parameters	Process 1	Process 2
Process 2 (calculated)	E	163	205
$w_1 = 25$	A	1.6×10^8	3.5×10^9
$w_2 = 75$	n	0.7	0.9
	w	25.1	74.9
Process 2 (calculated)	E	158	208
$w_1 = 50$	A	7.9×10^7	5.2×10^9
$w_2 = 50$	n	0.6	0.9
	w	50.2	49.8
Process 2 (calculated)	E	159	205
$w_1 = 75$	A	9.4×10^7	3.5×10^9
$w_2 = 25$	n	0.6	0.9
	w	74.7	25.3
Process 2 (experimental)	E	164	196
$w_1 = 25$	A	1.9×10^8	1.1×10^9
$w_2 = 75$	n	0.7	0.9
	w	23.7	76.3
Process 2 (experimental)	E	165	204
$w_1 = 50$	A	2.0×10^8	3.2×10^9
$w_2 = 50$	n	0.7	0.9
	w	50.2	49.8
Process 2 (experimental)	E	165	205
$w_1 = 75$	A	1.9×10^8	3.5×10^9
$w_2 = 25$	n	0.7	0.9
	w	75.6	24.4

regression for the two processes present good accordance with the theoretical values. The calculated mass fractions of the reacting components present only minimum deviations from the expected values.

5. Conclusions

The presented results show that a simultaneous calculation of the activation energy, frequency factor, and reaction order from a single TG curve by the direct non-linear regression of the kinetic equation is possible. Though, the calculated values do not have a clear physical meaning, they represent an objective description of the thermogravimetric curve and characterize the processes taking place.

The proposed method of calculation was applied for determining the kinetic parameters of both the simulated and experimental TG curves for a single process. The results of the calculations were compared with the values obtained by means of the methods by Coats and Refern [20], Horowitz and Metzger [21], Freeman and Carroll [22], and by Vachuska and Voboril [23]. It can be concluded from this comparison that the results are in a very good mutual accordance except for the method by Horowitz and Metzger that gives systematically higher values of all the parameters.

The proposed method was also verified from the standpoint of the dependence of the calculated parameters on random errors of the experimental data. Respecting the results of the comparative methods, the method of non-linear regression appears to be the best from this point of view. It is characterized by good stability of the solution even for high errors of the experimental data.

The method of non-linear regression was utilized as well for the determination of the kinetic parameters of the two processes whose TG curves are partly overlapping. The simulated TG curves as well as the combined simulation + experiment curves were utilized for the calculation. The results showed that the linearization elimination at the calculation enables to determine both the kinetic parameters for overlapping processes and the mass fractions of the reacting substances, which is not possible by means of the testing methods [20–23].

Acknowledgements

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