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APPLICATION OF NON-LINEAR REGRESSION METHODS FOR THE ESTIMATION OF COMMON KINETIC PARAMETERS FROM SEVERAL THERMOANALYTICAL CURVES

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Abstract

Novel methods of unified evaluation of two (or more) thermogravimetric curves have been worked out on the basis of known non-linear parameter estimating procedures (Gauss-Newton-Marquardt-type regression and the direct integral method of Valkó and Vajda were adapted). Their ability to provide estimate for common kinetic parameters of several TG (m–T) or DTG (dm/dt–T) curves were tested for pairs of curves of different heating rates, and for repeated curves of the same heating rate, obtained for the decomposition of $CaCO_3$ in open crucible. In these cases the Arrhenius terms and the n-th order model functions were assumed. The fitting ability of estimations made for single curves and for pairs of curves sharing different number of parameters, was judged on the base of residual deviations (s_{res}) and compared to the standard deviation of the measurements.

In the case of different heating rates, the two curves could not be described with the assumption of three common parameters, because of the minimum residual deviation was very high. However, sharing of activation energy and preexponential term only, and applying different exponents for the two curves, provided a satisfactory fit by our methods. Whilst in the case of repeated curves, we could find such a common three-parameter set, which has a residual deviation comparable with the standard deviation of the measurements.

Because of their flexibility (taking into account the variable number of common parameters and the versatile forms of model equations), these methods seem to be promising means for unified evaluation of several related thermoanalytical curves.

Keywords: mulitple scans, non-linear regression methods, residual deviation

Introduction

Using several curves of different heating rates in one evaluation process has a tradition in thermal kinetics. This type of methods is often mentioned as mul-

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tiple scan methods or multiple heating rate methods. Various well-known methods belong to this family, e.g. Kissinger's maximum rate method [1], Ozawa-Flynn-Wall analysis [2, 3] using Doyle's approximation, and the isoconversion method [4]. One of the main advantages of this kind of kinetic calculations is that they unify information from several thermal measurements. More experiments represent more information about the reaction in question.

These methods require only relatively simple mathematical tools, only logarithmic – linear plots, linear regression. According to Kissinger lg $(\beta_i/(T_{p,i})^2)$ values are plotted *vs.* $1/T_{p,i}$, where $T_{p,i}$ is the temperature belonging to the maximum rate of reaction at heating rate β_i. The Ozawa-Flynn-Wall analysis plots lg β_i, while the isoconversion method plots lg $d\alpha_i/dt$ values belonging to the same degree of conversion (α_i) but to various heating rates (β_i) as a function of the corresponding $1/T_i$. Then a straight line is fitted for the points, and an activation energy value is calculated from the slope of the line.

This energy value generally considered as a model-free estimation of the formal activation energy, i.e. none of the types of function $f(\alpha)$ is specified for describing the dependence of the rate of reaction on the conversion (α). The temperature dependence is considered corresponding to the Arrhenius equation. The latter two methods [2–4] provide the activation energy values E_i belonging to a series of reacted fraction α_i. Change in the energy values may reflect some changes in the kinetics.

The linear regression can be carried out in a relatively reliable way having at least 4–5 points. That is, at least 4–5 different heating rates have to be applied. Slow heating or wide range of temperature may result in long experimental times. Different heating rates may cause significant changes in the reaction pathways and mechanisms.

Our methods process two (or more) data series of samples, measured either under different or the same experimental conditions. They give estimations for all of the kinetic parameters involved in the rate equations of samples. They allow to apply both different and common parameters or models for several scans of samples. For example, they provide an opportunity to test different kinetic functions for different heating rates, or to determine shareable formal parameters of two (or more) scans at the same heating rate, etc. Comparisons can be made on the basis of unified residual deviations between the experimental and corresponding fitted curves.

Description of the new calculation methods

Our methods are based on non-linear regression algorithms, so they are able to give estimate for three or more parameters. This ability is important during modelling, for the number of parameters of two or more curves can be greater than three. For example, if we apply the Arrhenius equation and the *n*-th order than three. For example, if we apply the Arrhenius equation and the n-th order model for two curves of very different heating rates, we shall have six parameters, A_1, E_1, n_1, A_2, E_2, n_2.

$$\frac{\mathrm{d}\alpha_1}{\mathrm{d}t}=A_1\exp\left(-\frac{E_1}{RT_1}\right)(1-\alpha_1)^{n_1};\qquad \frac{\mathrm{d}T_1}{\mathrm{d}t}=\beta_1$$

$$\frac{\mathrm{d}\alpha_2}{\mathrm{d}t}=A_2\exp\left(-\frac{E_2}{RT_2}\right)(1-\alpha_2)^{n_2};\qquad \frac{\mathrm{d}T_2}{\mathrm{d}t}=\beta_2$$

Assuming that some of the parameters are common, the number of unknown parameters can be reduced to three (A, E, n) if the same kinetics is expected.

The applied algorithms allow using various kinds of $f(\alpha)$ model equations (listed e.g. in Refs [5, 6]. The investigations are not restricted to one special type of model. For example, instead of n-th order family $f(\alpha)=(1-\alpha)^n$, one can try the Avrami-Erofeev model family $f(\alpha)=(1-\alpha)\,[-\ln(1-\alpha)]^n$, etc.

For DTG data a Gauss-Newton-Marquardt-type non-linear regression was used [7], whilst for TG curves a differential equation set identifying method was applied. The latter method is called direct integral method established and implemented by Valkó and Vajda [8]. It is based on the integral form of the differential equation set and handles the functions as natural cubic interpolating splines. The use of splines provides an opportunity to work on non-smoothed data, and allows the estimation of residuals without repeated time consuming numerical solution of the original differential equation set, that is integration is accomplished only once, at the end of whole iterative process. The integration itself is carried out by a numerical method of special reliability.

Both estimation procedures work iteratively in order to reach the least square sum of differences between the estimated and the experimental curves. The finally reached squares of residual differences are summed and the so-called residual deviation, s_{res} is calculated:

$$s^2_{\mathrm{res,\,TG}}=\frac{\sum\limits_{j=1}^{nc}\sum\limits_{i=1}^{nm_j}(\hat{\alpha}_{i,j}-\alpha_{i,j})^2}{\sum\limits_{j=1}^{nc}(nm_j-np_j)},\quad \text{or}\quad s^2_{\mathrm{res,\,DTG}}=\frac{\sum\limits_{j=1}^{nc}\sum\limits_{i=1}^{nm_j}\left(\frac{\mathrm{d}\hat{\alpha}_{i,j}}{\mathrm{d}t}-\frac{\mathrm{d}\alpha_{i,j}}{\mathrm{d}t}\right)^2}{\sum\limits_{j=1}^{nc}(nm_j-np_j)}$$

where nc is the number of curves involved,
nm_j is the number of measured points at the j-th curve,
np_j is the number of estimated parameters at the j-th curve,

$d\alpha_{i,j}/dt$ is the calculated rate of conversion of the i-th point at the j-th curve, $d\alpha_{i,j}/dt$ is the measured rate of conversion of the i-th point at the j-th curve.

Fit of the different curves calculated according different assumptions can be evaluated using these residual deviations, because s_{res} can serve as a measure of the quality of fit. The use of the squared sum of residuals in the evaluation has been proposed by several authors, e.g. Várhegyi [9, 10]. The above defined residual deviations can serve as an absolute quantity, in wide scope of comparisons. The degree of freedom of estimation,

$$\sum_{j=1}^{nc} (nm_j - np_j)$$

in the denominator, makes s_{res} comparable for various estimations with different numbers of estimated parameters or measured points.

Application of the new methods for measured curves

Thermal experiments and data collection

The thermogravimetric TG (m–T) curves of $CaCO_3$ were measured at heating rates of 10 and 20 deg·min^{-1} on a DuPont 990 Thermal Analysis System. The decomposition of samples of about 6 mg were carried out in flowing Ar atmosphere (10 l/h) in an open platinum crucible. In both cases 21 m–T data points were collected in the interval of weight changes (550–750, or 600–800°C, respectively) equidistantly by 10°C. Then other two parallel measurements were carried out at 20 deg·min^{-1} heating rate, and again 21–21 corresponding m–T pairs were used in the calculation.

Results and discussion

Evaluation of a single curve: changes of parameters during iteration

First, the operation of the direct integral method is demonstrated on the evaluation of a single curve. Let us use the measured data of $CaCO_3$ at the heating rate of 20 deg·min^{-1} and the n-th order model family $f(\alpha) = (1 - \alpha)^n$. In this case we have three unknown parameters (A, E, n).

Starting from an initial set of values this non-linear method provides new and new sets of parameters, meanwhile the squared sum of the residuals and the above defined residual deviations are reduced successively. The iteration process stops if the relative change of parameter vector shows a very small selected value, e.g. $\varepsilon = 10^{-6}$, indicating that a minimum of the squared sum reached.

Theoretically this point corresponds to a local minimum, but we can consider it as the expected minimum if other iterations starting from different initial values lead to the same point.

The results of two iterative processes using extremely different initial values are shown in Tables 1 and 2. They contain values of the kinetic parameters and the residual deviation of the initial, the final and some selected steps. Within a few steps the initial deviations reduced to the order of magnitude of experimental standard deviation, that is the procedure first seems to work in a robust way. The further steps refine the estimation, but it takes a long time to find a minimum, that is the procedure converges very slowly, meanwhile the residual deviation of the estimated curves also changes slowly. Both iteration processes stopped at the same values of parameters (relative change $\varepsilon = 10^{-6}$ was used as criterion). Thus this parameter set can be accepted as a final estimate of kinetic parameters, providing the best fit with the least residual deviation $s_{res}=0.0074$ (Fig. 1).

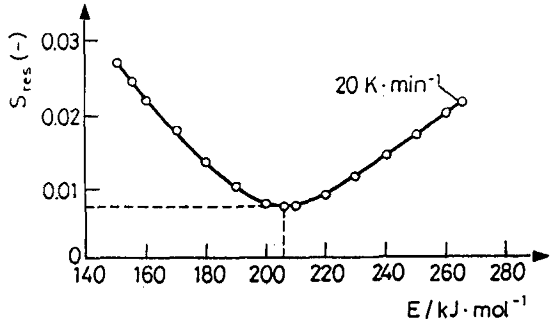

Fig. 1 Decrease of residual deviation obtained during the iterations executed by the direct integral method started from two different initial parameter set for the decomposition curve of $CaCO_3$ at heating rate of 20 deg·min^{-1}. Points corresponding to the initial parameter set (they should be situated to the left of the first and to the right of the last point somewhere up), are not described in this Figure (see data of Tables 1 and 2). The dashed lines indicate the parameter set to which both of the iterations independently converge

The great number of iteration steps needed in spite of the robustness of the method can be interpreted by the so-called 'kinetic compensation effect'[*]

In our case this effect occurs as a strong correlation of the series of estimate activation energies with the series of the corresponding preexponential factors,

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[*] The activation energy and the logarithm of preexponential factor estimated for similar samples, or for a sample measured under different conditions [11, 12], or evaluated by different mathematical methods or with different model assumptions [13, 14] show a very strong linear correlation, called as kinetic compensation effect [5, 15, 16].

and even with the series of exponents as well, as can be seen in Fig. 2. They all, obtained even in different iterations, seem to be correlated with each other. The slow changes of residual deviation as a function of iteration steps are plotted on the Fig. 3., starting the iteration from the above two initial points.

Table 1 Estimated parameters and the corresponding residual deviations obtained in a single curve fitting for the decomposition curve of $CaCO_3$ at 20 deg·min^{-1} (Iteration 1)

Number of iteration steps	Preexponential factor / min^{-1}	Activation energy / kJ·mol^{-1}	Formal order n (–)	Residual deviation s_{res} (–)
0 (Initial guess)	$1.000\cdot10^{7}$	150.00	0.3500	0.1970
8	$1.618\cdot10^{7}$	150.06	0.4303	0.0271
49	$3.028\cdot10^{7}$	155.00	0.4557	0.0246
96	$5.688\cdot10^{7}$	159.97	0.4814	0.0222
137	$2.044\cdot10^{8}$	170.11	0.5347	0.0178
154	$7.162\cdot10^{8}$	179.99	0.5878	0.0136
181	$2.519\cdot10^{9}$	189.91	0.6423	0.0101
240	$9.063\cdot10^{9}$	200.02	0.6991	0.0078
376 (Final step)	$1.972\cdot10^{10}$	206.16	0.7343	0.0074

Table 2 Estimated parameters and the corresponding residual deviations obtained in a single curve fitting for the same experiment of $CaCO_3$ decomposition at 20 deg·min^{-1} as in Table 1, starting from absolutely different initial guess

Number of iteration steps	Preexponential factor / min^{-1}	Activation energy / kJ·mol^{-1}	Formal order n (–)	Residual deviation s_{res} (–)
0 (Initial guess)	$1.000\cdot10^{14}$	270.00	1.1000	0.3516
12	$3.424\cdot10^{13}$	265.10	1.0970	0.0218
21	$1.782\cdot10^{13}$	259.94	1.0640	0.0204
40	$5.066\cdot10^{12}$	250.00	1.0000	0.0174
62	$1.458\cdot10^{12}$	240.16	0.9383	0.0146
90	$4.120\cdot10^{11}$	230.17	0.8768	0.0117
131	$1.144\cdot10^{11}$	220.04	0.8158	0.0091
220	$3.221\cdot10^{10}$	210.03	0.7569	0.0075
238 (Final step)	$1.985\cdot10^{10}$	206.21	0.7346	0.0074

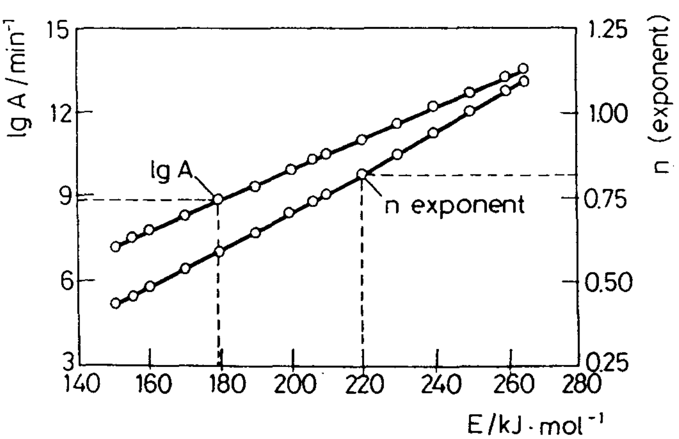

Fig. 2 Correlations of the estimated series of logarithm of preexponential factors and former orders n with the corresponding series of estimated activation energies obtained for $CaCO_3$ with 20 deg·min^{-1} heating rate, by the direct integral method (data of Tables 1 and 2)

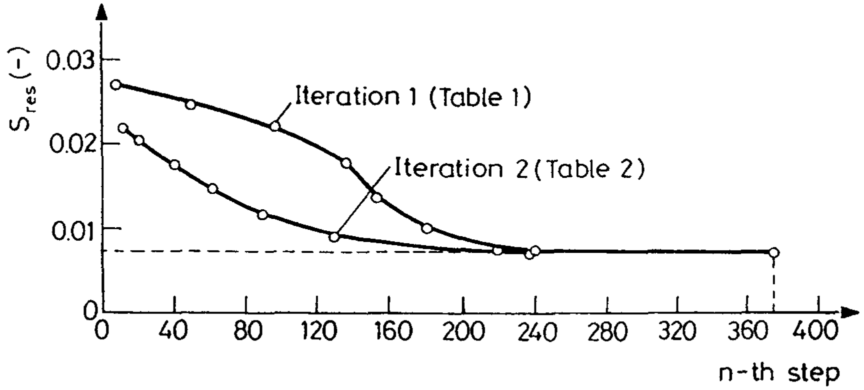

Fig. 3 The course of residual deviations as a function of the number of iteration steps (data of Tables 1 and 2)

Simultaneous evaluation of curves recorded with different heating rate

Figure 1 shows a plain valley and not a deep gap. From this range we considered only one parameter set as a result having the least residual deviation. Is this parameter set optimal for an other curve of a different or the same heating rate? Can we find common parameters providing satisfactory fit, at all? These questions can be answered using the proposed methods for the simultaneous (unified) evaluation of two (or more) curves. This way we could investigate the effect of common parameters on the estimations carried out for two curves of $CaCO_3$ obtained first at heating rate 10 and 20 deg·min^{-1}.

First, data recorded with 10 deg·min^{-1} were evaluated with the single-curve method. This provided a parameter set of almost the same minimum residual deviation. The estimated activation energy was nearly the same, while exponent *n* was significantly different from the values of obtained for heating rate of 20 deg·min^{-1}. This fact may indicate that all of the three parameters cannot be common for the two curves.

Then the double-curve method was used to identify the number of common parameters for these two curves. Three possible cases were examined. First all of the three parameters were assumed to be shareable. The combined evaluation process resulted in a significantly different parameter set from the above two, and a very large minimal residual value, showing bad fit (Table 3 and Fig. 4). This result cannot be accepted on the basis of experimental standard deviation of 0.01–0.02, in dimension of conversion.

Table 3 The estimated parameters and the corresponding residual deviations obtained in different ways by the single and double-curve methods for decomposition of $CaCO_3$ at heating rate of 20 and 10 deg·min^{-1}

Method of fitting and the involved curve(s)	Preexponential factors / min^{-1}	Activation energy / kJ·mol^{-1}	Formal order n (–)	Residual deviation s_{res} (–)
Single/3 (20 deg·min^{-1})	$1.985\cdot10^{10}$	206.2	0.734	0.0074
Single/3 (10 deg·min^{-1})	$3.763\cdot10^{10}$	210.5	0.469	0.0078
Double/3 (3 common parameters)	$4.126\cdot10^{7}$	157.6	0.419	0.0382
Double/4 (20 deg·min^{-1})	$7.880\cdot10^{9}$	198.7	0.718	0.0096
(10 deg·min^{-1})			0.375	
Double/5 (20 deg·min^{-1})	$2.629\cdot10^{10}$	208.4	0.747	0.0075
(10 deg·min^{-1})	$2.871\cdot10^{10}$		0.458	

Next the exponents were considered to be different for the two curves, while the activation energy and the preexponential factor remained common. So in this case there were 4 parameters (A, E, n_1 and n_2) involved in the united procedure for the two curves. The iteration resulted in a satisfactorily good parameter set, not far from the individual solutions considering both the values of the parameters and the reached minimal residual deviations as well.

In the third step, considering activation energy to be the only common parameter and the preexponential factors and exponents to be different for the two curves, we carried out five-parameter estimation. The result of this kind of estimation could be considered as a superposition of the two individual estimations carried out earlier for the two curves. The reached residual deviation had the same value as in the individual case and the estimated activation energy was between the two of the individual activation energies obtained. This common activation energy can be considered as a kind of model-free estimation, ignoring the other 4 parameters estimated for the full description of the curves.

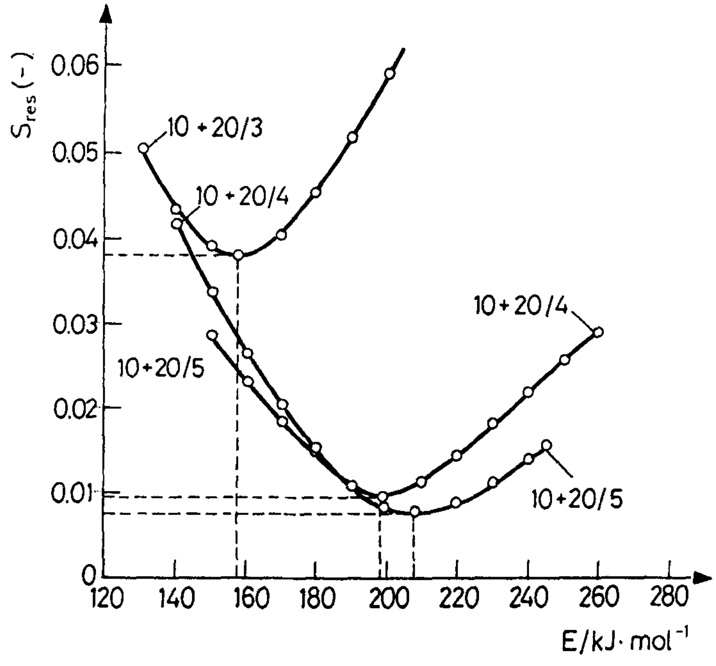

Fig. 4 Residual deviations ('10 + 20/3', '10 + 20/4', '10 + 20/5') as a function of the estimated common activation energy obtained by double-curve fittings for the curves of $CaCO_3$ decomposition with heating rates of 20 and 10 deg·min^{-1}, using 3, 2 and 1 common parameters, respectively

The final estimates and the corresponding residual values are summarised in the Table 3 for the mentioned cases. The curves of residual deviations obtained by the double-curve method is shown in Fig. 4.

Our conclusion is, that these two curves of decomposition of $CaCO_3$ at different heating rate can be evaluated together by sharing the activation energy and the preexponential factor in the conventional kinetic equations, but not the exponent. The two different exponents required indicate that the change of the heating rate has caused significant changes in the kinetics of the reaction, most likely through the variation of the rate and conditions of heat and mass transport processes. These estimations supported the model assumptions (i.e., the applicability of the formal order model).

Calculations from repeated curves

We also applied our methods for common evaluation of repeated scans at heating rate of 20 deg·min^{-1}. The resulted residual deviations of the single and double-curve estimations for two repeated curves, plotted against the estimated activation energy can be seen on the Fig. 5. The minimal levels of the residual deviations are less then 0.02, the observed standard deviation of measurements, even if three common parameters were applied for the repeated curves. That is, these estimated curves are as close to the experimental ones as the experimental ones to each other.

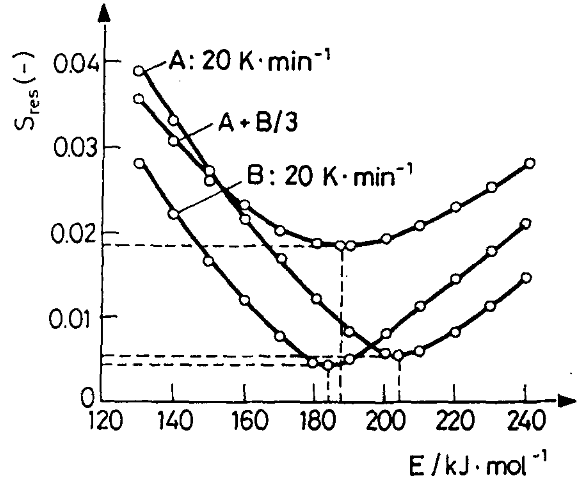

Fig. 5 Residual deviations as a function of the estimated activation energy obtained by the direct integral method for the curves of repeated decomposition of $CaCO_3$ at heating rate of 20 deg·min^{-1} using both single ('A' and 'B') and double-curve fittings (using 3 common parameters in the latter case, 'A + B/3')

Table 4 The estimated parameters and the corresponding residual deviations obtained in different ways by the single and double-curve methods for repeated decompositions of $CaCO_3$ at heating rate of 20 deg·min^{-1}

Method of fitting and the involved curve(s)	Preexponential factors / min^{-1}	Activation energy / kJ·mol^{-1}	Formal order n (–)	Residual deviation s_{res} (–)
Single/A (20 deg·min^{-1})	$1.868 \cdot 10^{10}$	204.3	0.606	0.0053
Single/B (20 deg·min^{-1})	$1.558 \cdot 10^{9}$	184.1	0.525	0.0043
Double/A+B/3 common parameters	$2.683 \cdot 10^{9}$	188.7	0.539	0.0186

The obtained parameters for the repeated curves are summarised in Table 4. Considering only the activation energies, they are within a 20–21 kJ/mol wide range of values, showing about 10% relative uncertainties. These values depend mostly on the repeatability of the measurements themselves.

Conclusions

Generally speaking, the non-linear estimating methods are good tools of mapping the parameter space for a reasonably acceptable set of kinetic parameters, because of their versatile applicability. They allow an evaluation of the curve fit on the basis of residual square sums or residual deviations in comparison with the experimental standard deviation. In addition these methods within their own scope show that all the estimated parameters are strongly correlated, i.e. at the same time more than one curve can be fitted with similar accuracy for an experimental curve.

To improve the reliability of the estimations, two (or more) curves can be involved in a unified curve-fitting process. We established new methods, which need two (or more) dynamic runs and fully evaluate them together. When two curves are involved, our method may spare some experimental time compared with classical model-free activation energy estimating methods, like the isoconversion method, or Ozawa-Flynn-Wall analysis, which require at least 3 or 4 dynamic runs.

Furthermore our methods evaluate the full curves together. Comparing the reached minimum residual deviations to the experimental standard deviation, we could detect the change of reaction details for different heating rates, and the lack of such changes in the case of repeated curves. That is, the number of shareable common parameters can give further information about the merit of model assumed.

Generalisation of our method provides an opportunity to estimate common parameters of several related thermal curves within one and the same numerical procedure.

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Zusammenfassung — Auf der Basis bekannter nichtlinearer Parameter-Schätzungsverfahren (Adaption der Gauss-Newton-Marquardt-Regression und der direkten Integrationsmethode von Valkó und Vajda) wurden neue Methoden zur gemeinsamen Auswertung von zwei (oder mehr) thermogravimetrischen Kurven ausgearbeitet. Ihre Fähigkeit zur Schätzungen von gewöhnlichen kinetischen Parametern einiger TG (*m*-*T*)- oder DTG (d*m*/d*t*-*T*)-Kurven wurde für Kurvenpaare unterschiedlicher Aufheizgeschwindigkeit und für wiederholte Kurven bei gleicher Aufheizgeschwindigkeit an der Zersetzung von $CaCO_3$ in einem offenen Ofen getestet. In diesen Fällen wurden Arrhenius'sche Ausdrücke und Modellfunktionen *n*-ter Ordnung vorausgesetzt. Die Fitting-Fähigkeit der Schätzungen für Einfachkurven und für Kurvenpaare mit einer unterschiedlichen Anzahl von Parametern wurde auf der Basis der residualen Deviationen (s_{res}) überprüft und mit der Standarddeviation der Messungen verglichen.

Im Falle unterschiedlicher Aufheizgeschwindigkeiten konnten die zwei Kurven unter Annahme von drei gewöhnlichen Parametern nicht beschrieben werden, da die minimale residuale Deviation sehr hoch war. Die Anwendung von nur Aktivierungsenergie und präexponentiellem Faktor sowie von verschiedenen Exponenten für die beiden Kurven lieferte ein zufriedenstellendes Fitting unserer Methode. Dagegen konnten wir im Falle der wiederholten Kurven ein solches Tripel üblicher Parameter finden, welches eine vergleichbare residuale Deviation wie die Standarddeviation der Messungen aufweist.

Aufgrund ihrer Flexibilität (unter Berücksichtigung der unterschiedlichen Anzahl gewöhnlicher Parameter und der flexiblen Form der Modellgleichungen) scheinen diese Methoden vielversprechende Mittel zur gemeinsamen Auswertung einiger verwandter thermoanalytischer Kurven zu sein.