

DETERMINATION OF KINETIC PARAMETERS IN TG AND DSC BY MEANS OF DIRECT OVERALL EVALUATION OF SIMPLE AND COMPLEX REACTIONS

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For kinetic evaluation by TG and DSC of simple and complex reactions we used a direct fit on the basis of TG differential equations and DSC non-linear equations. The advantages of an overall evaluation, i.e. the simultaneous inclusion of all data sets at different heating rates, are described. TG and DSC measurements of the dehydration of calcium oxalate monohydrate and the decomposition of calcium oxalate are used as examples.

Keywords: determination of kinetic parameters, DSC, overall evaluation, TG

Theory

The direct fitting of data of thermogravimetry (TG) on the basis of the ordinary differential equations

$$\frac{dA}{dT} = -\frac{k_0}{q} \exp\left(-\frac{E_A}{RT}\right) A^n \quad (1a)$$

or

$$\frac{dA}{dt} = -k_0 \exp\left(-\frac{E_A}{R(T_0 + qt)}\right) A^n \quad (1b)$$

$$A = (1 - \alpha); \quad \alpha = \frac{M_0 - M_t}{M_0 - M_\infty}; \quad q = \frac{dT}{dt}$$

where m = mass, α = degree of decomposition; q = heating rate; $T = T_0 + qt$ for a linear heating rate and of data of differential scanning calorimetry (DSC) on the basis of non-linear equations

$$\frac{d\dot{Q}}{dt} = k_0 \exp\left(-\frac{E_A}{R(T_0 + qt)}\right) \left(\frac{c_0}{Q_\infty}\right)^{n-1} \left(Q_\infty - \int_0^t \dot{Q} dt\right)^n \quad (2)$$

where $Q_\infty = \int_0^\infty \dot{Q} dt$ (total heat of reaction); $\dot{Q} = \frac{dQ}{dt}$ (heat flux)

is an effective method for obtaining information on activation energy (E_A), frequency factor (k_0) and reaction order (n). Compared to the usual methods, the major advantage of fitting data by means of Eqs (1) or (2) to obtain kinetic parameters is the direct utilization of the primary measured data. For the non-linear optimization we applied a trust-region method with Marquardt-routine* [3]. The integration was achieved by means of the Runge-Kutta four-step calculation. For determining the DSC partial curves we used cubic spline functions. In general, our programmes can be used on all personal computers which are IBM compatible.

It should be mentioned that q can also be a non-linear function of temperature. As normal, we used a linear heating rate. Unfortunately, thermoanalytical measurements of solids are connected with random or systematic errors related to simplification of the kinetic model used and further difficult problems such as heat transport and temperature gradients in the sample [5]. Therefore it is desirable to improve the reliability of the kinetic constants. This is possible with an overall evaluation of the data [1, 2]. For the usual fitting we need a set of TG or DSC data at a single heating rate q . By overall evaluation is meant the simultaneous inclusion of all data sets at different heating rates q_i . This evaluation is performed using Eqs (1b) and (2).

From a theoretical point of view the overall evaluation gives, in connection with statistical tests, correct kinetic constants, i.e. parameters which are consistent with all data in the data sets obtained on the basis of the model used. For an overall fitting we need data sets for two or more heating rates. The confidence interval as well as a modified F -test confirm the acceptability of the chosen model and the reliability of its parameters. For calculating the zero variance σ_0^2 , individual sets of measurements at different heating rates were treated as repeat measurements. Then this kind of modified F -test took the form:

$$F_{\text{exp}} < F(\alpha, f_1, f_2)$$

$$F_{\text{exp}} = \frac{\sigma_R^2(f_1)}{\sigma_0^2(f_2)}$$

* We thank Dr. V. Tiller, University of Hannover, for making his Turbo-Pascal-Programmes for parameter estimation in ordinary differential equations available to us.

$$\delta_o^2 = \frac{FQS_o}{nf_2}$$

$$FQS_o = \sum_{j=1}^m \sum_{k=1}^n (y_{jk} - \hat{y}_{jk})^2$$

where m = number of heating rates q_i , n = number of data at the set q_i , $f_2 = m-1$, $m > 2$.

*Analysis of experimental data**

Investigation of the decomposition of calcium oxalate to calcium carbonate and carbon monoxide at about 700 K by means of TG and DSC led to similar results (Tables 1 and 2), i. e. the TG single, the TG overall, the DSC single and the DSC overall evaluations led to kinetic parameters which had nearly the same confidence intervals. A simple first-order reaction could be confirmed. In general, the arithmetic means of the kinetic constants derived from different heating rates cannot be used because they could give constants which are incompatible with the experimental data. Here this fact is insignificant.

Table 1 Kinetic evaluation of TG data for the reaction $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$

$q/\text{deg}\cdot\text{sec}^{-1}$	$\ln k_o / \text{sec}^{-1}$	$E_A / \text{kJ}\cdot\text{mol}^{-1}$	$F\text{-test}$
$q_1 = 1/60$	36.11 ± 3.5	273.2 ± 21	
$q_2 = 1/20$	37.64 ± 2.9	270.3 ± 19	
$q_3 = 1/6$	39.40 ± 2.6	263.1 ± 17	
Overall	39.58 ± 9.1	267.4 ± 44	+

Table 2 Kinetic evaluation of DSC data for the reaction $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$

$q/\text{deg}\cdot\text{sec}^{-1}$	$\ln k_o / \text{sec}^{-1}$	$E_A / \text{kJ}\cdot\text{mol}^{-1}$	$F\text{-test}$
$q_1 = 1/60$	37.51 ± 2.8	259.1 ± 11	
$q_2 = 1/20$	38.10 ± 2.9	264.2 ± 13	
$q_3 = 1/6$	36.01 ± 3.1	266.0 ± 9.8	
Overall	36.76 ± 5.1	259.4 ± 37	+

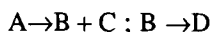
* We thank Dr. Dietrich Schultze, Berlin, for the TG (Setaram TAG 24) and DSC measurements (Setaram DSC 92)

A more complicated process is the dehydration of calcium oxalate monohydrate [2, 4]. Opfermann *et al.* [2] have shown that the TG measurements should be interpreted as a complex reaction consisting of two steps, a first-order reaction and a two-dimensional phase-boundary reaction. On the basis of a TG overall evaluation the combination of the steps was interpreted either as a consecutive reaction or as two independent reactions. The TG data were confirmed by both models.

Table 3 Kinetic evaluation of DSC data for the dehydration of calcium oxalate monohydrate as a consecutive reaction

$q/\text{deg}\cdot\text{sec}^{-1}$	$\ln k_{01} / \text{sec}^{-1}$	$E_{A1} / \text{kJ}\cdot\text{mol}^{-1}$	$\ln k_{02} / \text{sec}^{-1}$	$E_{A2} / \text{kJ}\cdot\text{mol}^{-1}$
$q_1 = 1/60$	44.3 ± 3.8	188.3 ± 9.6	19.5 ± 2.9	94.58 ± 8.4
$q_2 = 1/20$	42.8 ± 4.3	179.9 ± 11	21.8 ± 3.9	99.37 ± 9.1
$q_3 = 1/6$	40.2 ± 2.9	175.2 ± 8.9	20.4 ± 4.3	92.75 ± 10
Overall	42.0 ± 7.8	174.4 ± 24	22.45 ± 6.8	96.48 ± 28
		(<i>F</i> -test +)		

We follow the interpretation of Opferman *et al.* but we prefer the assumption of a consecutive reaction



According to this model we determined the kinetic parameters by means of the DSC single and DSC overall evaluation (Table 3) on the basis of the derived equations

$$\frac{dQ_1}{dt} = k_1 \left(Q_{\infty 1} - \int_0^t \dot{Q}_1 dt \right) \quad (3)$$

$$\frac{dQ_2}{dt} = 2k_2 \left(\frac{Q_{\infty 2}}{c_{\infty B}} (c_{0A} - c_A) - k_2 \int_0^t \dot{Q}_2 dt \right)^{1/2} \quad (4)$$

$$c_A = c_{0A} - \frac{c_{0A}}{Q_{\infty 1}} \int_0^t \dot{Q}_1 dt$$

$$c_B = c_{0A} - c_A - \frac{c_{\infty B}}{Q_{\infty 2}} \int_0^t \dot{Q}_2 dt$$

$$k_1 = k_{01} \exp(-E_{A1}/RT) ; \quad k_2 = k_{02} \exp(-E_{A2}/RT) ;$$

It can be seen that the calculated kinetic parameters are statistically secured; the DSC data are consistent with the model. The *F*-test may be used, but this is not absolutely necessary. The results are similar to those of the TG evaluation of

Opfermann *et al.* [2]. The small differences are due to the different measuring methods and the different kinds of equipment used.

In contrast to the TG evaluation, a reasonable DSC evaluation is only possible if the second step of the reaction begins distinctly later than the first. Then the first section of the experimental DSC curve fully corresponds to the partial curve of the first reaction. From this separated section we could derive, by means of the DSC relation (3), the amounts of k_{o1} and E_{A1} . As a rule, the kinetic constants are accessible if the partial curve until the first inflexion point is moderately influenced. Then the first partial curve can be simulated and by formation of the difference between the sum curve and the partial curve we obtain the partial curve of the second step.

It must be mentioned that the assumption of a three-dimensional phase boundary reaction for the second step of a reaction also leads to consistency between the DSC data sets and the chosen model. The confidence intervals are similar to those of the above model and the residuals are nearly identical. But the assumption of a two-dimensional phase-boundary reaction is more plausible.

In contrast to these models, a combination of a first-order decomposition reaction and a two- or a three-dimensional diffusion process is not statistically significant. An evaluation of a single q -data set leads only to a small discrepancy between the data and the model, but the overall evaluation leads to a great discrepancy. The determined kinetic parameters are not consistent with the chosen models.

Discussion

For the overall kinetic evaluation of thermoanalytical data sets of different heating rates it must be presumed that the mechanism of the reaction does not change and that the activation energy is not a function of temperature. For a more precise determination of the kinetic parameters we should also have some basic knowledge on the unfolding, i. e. the elimination of disturbing factors from the system of experimental conditions. But it can be observed that the direct fitting of thermoanalytical data always leads to more exact kinetic parameters compared to the usual methods of linearizing.

As a rule, the results of kinetic evaluation of reactions in the solid state should be assessed with some caution because the kinetics of these systems is frequently very complex.

References

- 1 J. Mentel and H. Anderson, *Thermochim. Acta*, 187 (1991) 121.
- 2 J. Opfermann, G. Wilke, J. Jung, W. Ludwig, S. Hagen, M. Gebhardt and E. Kaisersberger, *Thermische Analyseverfahren in Industrie und Forschung*, Friedrich-Schiller-Universität Jena 1991, pp. 51–79.

- 3 J. J. Moore, Numerical Analysis, G. A. Watson (ed.), Lecture Notes in Mathematics, 630, New York 1978, pp. 105–116.
- 4 Y. Masuda, Y. Ito, R. Ito and K. Iwata, Thermochem. Acta, 199 (1986) 205.
- 5 H. Anderson, Thermochem. Acta, 203 (1992) 515.

Zusammenfassung — Zur kinetischen Auswertung von einfachen und komplexen Reaktionen mittels TG und DSC wird auf der Grundlage von TG Differentialgleichungen und nichtlinearen DSC-Gleichungen ein direktes Fitting vorgenommen. Die Vorteile einer Gesamtauswertung, d.h. die gleichzeitige Einbeziehung aller Daten-Sets bei verschiedenen Aufheizgeschwindigkeiten, werden beschrieben. Als Beispiel werden TG- und DSC-Messungen bei der Dehydratation von Calciumoxalat-Monohydrat und der Zersetzung von Calciumoxalat verwendet.