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A new kind of parameter estimation of reactions under dynamic temperature programme

J. Mentel and H. Anderson

Department of Chemistry, University of Greifswald,
Soldtmannstr. 23, O-2200 Greifswald, Germany

Abstract

For kinetic evaluation of TG, DTA and DSC of simple and complex reactions we tried to apply a parameter adjustment by means of non-linear optimization (trust-region method with Marquardt-routine). Including all experimental data and using the differential equation systems, we found many advantages over the usual linearizing methods. The problems of consecutive and competing reactions as well as those with steady states (enzyme kinetics) were solved satisfactorily if two or more data sets with different heating rates are known. Supplementary use of other analytical methods are recommendable.

INTRODUCTION

In the last decades many physico-chemical investigations have been conducted in such a way that the processes and reactions were carried out under the effect of a defined temperature programme. In most cases a linear leading of temperature have been preferred. An important advantage over the isothermal working method is the possibility of complex kinetic evaluation in the special case of chemical reactions. Thus, not only the reaction rate but also its temperature dependence is obtained. Therefore, as a quantitative expression of the thermal analysis mode the reaction order n, the energy of activation E_A and the frequency factor k_0 are accessible.

Thermogravimetry TG, differential thermoanalysis DTA and differential scanning calorimetry DSC are the most frequently used methods of thermal

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analysis. On the basis of these basic techniques general kinds of kinetic evaluation of thermal analysis data are described. In contrast to the usual methods these methods are based on the direct utilization of the primary measured data. Thus a falsification of the kinetic parameters searched for by the wellknown approximation methods of linearizing over the whole experimentel range could be excluded. In the following we shall demonstrate this type of evaluation i.e. a direct estimate of parameters from differential equations and non-linear equation for simple and complex events.

1. KINETIC PARAMETERS OF SIMPLE CHEMICAL REACTIONS

An important prerequisite is that the reaction under investigation is homogeneous relative to its temperature and instantaneous composition. Mechanical homogenization for DTA- or DSC-probes is absolutely desirable, because an inhomogeneous medium makes all formulas approximative [1]. The connection between measured values (mass, difference of temperature, power of compensation) and the kinetic parameters is given by differential equations.

TG

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

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

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

m = mass
α = degree of decomposition
q = heating rate

As an usual TG-evaluation method the approximation of Coats and Redfern [2] is introduced:

$$\ln\frac{\int dA/A^n}{T^2} = \ln\frac{k_0R}{qE_A} - \frac{E_A}{RT} \tag{1a}$$

DTA

By the well known relations of Borchardt and Daniels [3]

$$\frac{dx}{dt} = k_0\exp(-\frac{E_A}{RT})(c_0-x)^n$$

$$\frac{dx}{dt} = \frac{c_0}{KA}\left(c_p\frac{\Delta T}{dt}+K\Delta T\right)$$

$$x = \frac{c_0}{KA}\left(c_p\Delta T + K\int_0^{t_i}\Delta T dt\right)$$

c_p = *heat capacity*
K = *constant of the apparatus*
c_0 = *initial concentration*
$\Delta T = T_1 - T_2$

$-\Delta H = KA$
x = *degree of conversion*
$A = \int_0^{\infty}\Delta T dt$

a differential equation is accessible:

$$\frac{d\Delta T}{dt} = \frac{k_0}{q}\exp\left(-\frac{E_A}{R(T_0+qt)}\right)\frac{K}{c_p}\left(\frac{c_0}{A}\right)^{n-1}\left(A-\int_0^{t_i}\Delta T dt-\frac{c_p}{K}\Delta T\right)^n-\frac{K}{c_p}\Delta T \tag{2}$$

An often applied DTA-evaluation according to Coats-Redfern-approximation [2] is

$$\ln\frac{\int_0^x dx/(c_0-x)^n}{T^2} = \ln\frac{k_0R}{qE_A}\left(1-\frac{2RT}{E_A}\right) - \frac{E_A}{RT} \tag{2a}$$

DSC

The differential equation taken as a basis follows directly from equation (2) because heat transition can be omitted:

$$\frac{dQ}{dt} = \frac{k_0}{q}\exp\left(-\frac{E_A}{R(T_0+qt)}\right)\left(\frac{c_0}{Q_\infty}\right)^{n-1}\left(Q_\infty-\int_0^{t_i}\dot{Q}dt\right)^n \tag{3}$$

$$Q_\infty = \int_0^\infty \dot{Q}dt \quad (\textit{total heat of reaction})$$

$$\dot{Q} = \frac{dQ}{dt} \quad (\textit{heat flux})$$

A frequent linearizing evaluation is

$$\ln\frac{\dot{Q}}{(Q_\infty - \int_0^{t_i}\dot{Q}dt)^n} = lnk_0 - \frac{E_A}{RT} \tag{3a}$$

All the three basic equations (1-3) are ordinary differential equations of first order. In order to achieve an optimal adjustment of the kinetic constants via the primary data, we need a robust programme for parameter estimation in ordinary differential equations. We applied a trust-region-method including Marquardt routine [4]. Integration was performed by means of a Runge-Kutta four-step calculation and the Gear BDF-method [5][1]. Since we have to consider differential equations it is necessary to optimize and integrate for every step of integration. Although equation (3) is formally of the same character as equation (1) and (2) it can also be considered as a non-linear equation because the compensating heat flux dQ/dt has been measured directly. For the same reason it is advisable to adjust the kinetic parameters of DSC-results directly by means of non-linear-regression.

The equations (1a, 2a, 3a) represent frequently used linearizing evaluation methods. Here, the order of reaction must be pretended or found out by an optimization separately. The formula (1a, 2a) contain an approximation for the so-called exponential integral. Therefore an exact linearization even of an error-free data set is impossible [6].

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[1] We have to thank Mr. Dr. V. Tiller of the Martin-Luther-University Halle for making the Turbo-Pascal-Programmes available.

For a direct estimate of parameters a prediction of starting values is requisite. The region of convergence becomes lower with increasing data scattering, but it is still sufficient for an unproblematic evaluation at moderate scattering (e.g. standard deviation $\sigma=0.003$). As a first orientation for TG and DTA should hold:

$\log(k_0/q)$ ± 1
E_A ± 15%
n ± 0.5

If the real parameters are $\log(k_0/q)=6$, $E_A=120$ kJmol^{-1}, $n=1$, $\sigma=0.003$, then the start values $\log(k_0/q)=7$, $E_A=140$, $n=1.5$ will produce convergence with certainty. For DSC evaluation the range of convergence is considerably larger. In cases with a difficult choice of starting values it is possible to compare simulated with measured data so that the quality and the influence of the starting values can be estimated. With respect to the heating rate there is generally no limitation as far as q is given as a defined function of time.

For a distinction between the models we performed simulations including data of different heating rates to asses the admissibility and the reliability of the evaluation on the one side and the proposed model on the other. For the evaluation of real experimental curves under different heating rates it must be presumed that the mechanism of reaction does not change and that E_A is not a function of temperature. Then the simulation led to the following results:

If an inappropriate model is used, data from a single heating experiment yield differing parameters in dependence on the position of the chosen data. Therefore the data analysis of a single data set produced parameters which allowed to recognize a wrong model only in limitation. Especially the arithmetic mean values of the kinetic constants derived from different heating rates cannot be used because they could give constants which are incompatible with the experimental data.

In the case of an overall-evaluation i.e. the simultaneous processing including of all the data of different heating experiments Opfermann proposed this so-called global analysis [7]. In extension to it we found that only two unequal heating rates are enough for a comprehensive kinetic description. The greater the difference of the included q-values, the more remarkable is the deviation of the individual from the overall-evaluation if the model is unrealistic.

The interval of confidence as well as a modified F-test indicate the degree of acceptability of the chosen model and the reliability of its parameters. To calculate the zero variance σ_0^2, the individual sets of measurements at different heating rates have been treated as repeated measurements. Thus, this kind of modified F-test took the form:

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

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

$$\sigma_0^2 = \frac{FQS_0}{nf_2}$$

$$FQS_0 = \sum_{j=1}^{m}\sum_{k=1}^{n}(y_{jk} - \hat{y}_{jk})^2$$

m = *number of heating rates* q_i

n = *number of data per set* q_i

$f_2 = m-1$

$m > 2$

The results of model distinction will be demonstrated using the following example:

TG-data were simulated for a 3-dimensional diffusion (Ginstling Brounshtein equation) in four sets of computer experiments at different heating rates with $\ln k_0 = 23$, $E_A = 230$ kJmol^{-1}, $\sigma = 0.003$. These data sets were used to distinguish the correct model 1 from the incorrect model 2, i.e. a chemical reaction of nth order. The calculations were made for an individual as well as overall-evaluation.

Model 1:
$$\frac{dA}{dt} = \frac{3k_0\exp\left(-\frac{E_A}{R(T_0+qt)}\right)}{2(A^{-1/3}-1)}$$

Model 2:
$$\frac{dA}{dt} = -k_0\exp\left(-\frac{E_A}{R(T_0+qt)}\right)A^n$$

Table 1
Data of model 1 calculated as model 2 in individual evaluation yield the following kinetic constants:

q_i/Kmin^{-1}	lnk$_0$(s^{-1})	E$_A$/kJmol^{-1}	n
q_1 = 1.0	8.491	108.4	0.439
q_2 = 2.5	8.161	108.6	0.439
q_3 = 5.0	7.837	108.7	0.438
q_4 =10.0	7.391	108.8	0.437

A superficial consideration could mislead us to calculate arithmetic means and thus to confirm a non-real model or unreliable parameters, using the overall-evaluation, however this false conclusion is not possible.

Table 2
Overall-evaluation of the data of model 1 as model 2

q	lnk$_0$	E$_A$/kJmol^{-1}	n	residual
q_{12}	16.38	161.0	1.490	0.177
Δ12	5.90	39.9	0.780	
q_{14}	24.26	213.4	2.367	0.228
Δ14	5.21	33.9	0.840	
q_{1234}	24.26	213.6	2.367	2.301
Δ1234	35.91	233.5	5.701	

Δ : The difference between the higher and lower value of the kinetic parameter at a confidence intervall of 95%

q_{1234}: overall-evaluation including the four heating rates

With regard to different q-values we found markedly changed parameters which could not be secured statistically. Moreover, the residual is too high. But the overall-evaluation of the data sets of q_1 and q_4 leads to nearly the same parameters as those of q_1, q_2, q_3 and q_4. In contrast to what is stated the overall-evaluation on the basis of the correct model produced only the expected parameters, which is reflected in the secured confidence interval.

Table 3
Overall-evaluation of the data of model 1 as model 1

q	$\ln k_0$	E_A/kJmol^{-1}	residual
q_{1234}	23.09	230.5	0.02
Δ1234	0.19	0.7	

2. KINETIC PARAMETERS OF COMPLEX CHEMICAL REACTIONS UNDER HOMOGENEOUS CONDITIONS

2.1. ENZYME KINETICS

These considerations are limited to the mechnism of Michaelis-Menten

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

if steady state is reached rapidly. From

$$\frac{dc(p)}{dt} = -\frac{dc(s)}{dt} = k_2 c(ES)$$

follows directly a reaction of 0th order i.e. c(ES) = constant.

$$\underline{DSC:} \quad \dot{Q} = k_{02}\frac{Q_\infty}{c_{ES}}\exp\left(-\frac{E_{A2}}{RT}\right) \qquad \textit{resp.} \qquad (4)$$

$$\ln\dot{Q} = \ln\left(k_{02}\frac{Q_\infty}{c_{ES}}\right) - \frac{E_{A2}}{RT}$$

$$\underline{DTA}: \quad \Delta\dot{T} = k_{02}\frac{K}{c_p}\frac{A}{c_{ES}}\exp\left(-\frac{E_{A2}}{RT}\right) - \frac{K}{c_p}\Delta T \tag{5}$$

Because of higher accuracy and simpler evaluation DSC-measurements should be preferred to DTA. Equation (4) is only exact valid, if c(ES) is constant i.e. also without temperature dependence according to the postulation $\Delta c_p = 0$. In contrast to the usual enzyme kinetic procedure measured points only in the steady state range should be applied. The non-steady state starting range will be unnoticed. Via equation (4) the activation energy E_{A2} of the rate determining step is accessible, but not k_{02} because c(ES) remains unknown. In any case the stability of the enzyme must remain unaffected.

2.2. ANALYSIS OF CONSECUTIVE REACTIONS EXCLUSIVELY FROM THERMAL MEASUREMENTS (DTA and DSC)

Instead of a general discussion of complex reactions let us demonstrate the effect by means of a relatively simple consecutive reaction
A --> B --> C . If only two steps of the reaction are considered an application to any ordinary and competing consecutive reactions is possible. For DTA experiments it was shown earlier [8] that a determination of kinetical parameters is possible in some cases for another kind of adjustment.

In the case of DTA the differential equations (6) and (7) are accessible which can be used for parameter adjustment.

$$\frac{d\Delta T_1}{dt} = k_1\left(\frac{KA_1}{c_p} - \Delta T_1 - \frac{K}{c_p}\int_0^{t_1}\Delta T_1 dt\right) - \frac{K}{c_p}\Delta T_1 \tag{6}$$

$$\frac{d\Delta T_2}{dt} = k_2\frac{KA_2}{c_p c_{\infty B}}\left(c_{0A} - c_A\right) - \frac{k_2}{c_p}\left(c_p\Delta T_2 + K\int_0^{t_1}\Delta T_2 dt\right) - \frac{K}{c_p}\Delta T_2 \tag{7}$$

$$
\begin{aligned}
\dot{c}_A &= -k_1 c_A \\
\dot{c}_B &= -\dot{c}_A - k_2 c_B \\
\Delta\dot{T}_1 &= k_1 \frac{KA_1}{c_{oA} c_p} c_A - \frac{K}{c_p}\Delta T_1 \\
\Delta\dot{T}_2 &= k_2 \frac{KA_2}{c_{\infty B} c_p} c_B - \frac{K}{c_p}\Delta T_2 \\
c_A &= c_{0A} - \frac{c_{0A}}{KA_1}\left(c_p \Delta T_1 + K\int_0^{t_i} \Delta T_1 dt\right) \\
c_B &= c_{0A} - c_A - \frac{c_{\infty B}}{KA_2}\left(c_p \Delta T_2 + K\int_0^{t_i} \Delta T_2 dt\right) \\
k_1 &= k_{o1} \exp\left(-\frac{E_{A1}}{RT}\right) \\
k_2 &= k_{02} \exp\left(-\frac{E_{A2}}{RT}\right)
\end{aligned}
$$

For DSC we found accordingly:

$$\frac{dQ_1}{dt} = k_1\left(Q_{\infty 1} - \int_0^{t_i} \dot{Q}_1 dt\right) \tag{8}$$

$$\frac{dQ_2}{dt} = k_2 \frac{Q_{\infty 2}}{c_{\infty B}}\left(c_{oA} - c_A\right) - k_2 \int_0^{t_i} \dot{Q}_2 dt \tag{9}$$

$$
\begin{aligned}
c_A &= c_{0A} - \frac{c_{0A}}{Q_{\infty 1}} \int_0^{t_i} \dot{Q}_1 dt \\
c_B &= c_{0A} - c_A - \frac{c_{\infty B}}{Q_{\infty 2}} \int_0^{t_i} \dot{Q}_2 dt
\end{aligned}
$$

A reasonable evaluation is only possible if the second step of the reaction begins distinctly later than the first i.e. the starting values of dx_2/dt, x_2 and c_{0C} should be equal to zero. Under these conditions the first section of the experimental curve fully corresponds to the partial curve of the first reaction. From this separated section we could derive, by means of the DTA relation (6) or DSC relation (8), the amounts of k_{01} and E_{A1} and in some cases n_1 or ΔH_1 too. As a rule, the kinetic constants are accessible if the partial curve until the first turning point is moderately influenced and the scattering of the curve is a low one. Namely 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. With the help of parameter estimation by equation (7) or (9) the amounts of k_{02}, E_{A2} and, in the general case also of n_2 were found. If n_2 could be pretended as far as desired, A_2 or $Q_{\infty 2}$ could be found too. Now ΔH is obtained by simple calculation.

Since at least four kinetic parameters should be derived from the total curve the results should, in any case, be confirmed by an experiment with another heating rate. An overall evaluation as described above must lead to parameters of nearly the same amount. If more than two heating rates are involved, the modified F-test is suitable. For evaluation we should pay special attention to the integration of the DTA- and DSC-partial curves. We used cubic spline-functions to approximate the run of the curves. Generally, our programmes can be used on all personal computers, a numerical processor is desirable but not necessary.

2.3. KINETIC EVALUATION OF COMPLEX REACTIONS USING THERMAL AND OTHER ANALYTICAL DATA

In any case a supplementation of the thermal data by independent analytical methods is desirable. Already for the simple consecutive reaction with early overlapping of the second step an evaluation exclusively on the basis of thermal signals is not possible. If, however, $c_A(t)$ can be followed up, then E_{A1} and k_{01} become accessible. In this way we are able to simulate the first partial curve. Thus also the second partial curve is always separable and the estimation of kinetic parameters is finished.

Provided that there are extensive analytical data in addition to the thermal ones, an evaluation including all data is to recommend if already the analytical measurements allow a full kinetic interpretation.

With respect to the accuracy of the thermal data the evaluation of the primary data should be followed by parameter estimation on the basis of the differential equation system. For constants inside the permissible interval of confidence we can regard the analytical and the thermal data consistent with one another.

Applications of the decribed method of evaluation to real complex reactions will be published in a forthcoming paper.

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