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# Comparison of different non-linear evaluation methods in thermal analysis[1]

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**Abstract**

With the aim of determining activation parameters, three computer programs have been investigated. Different routines for the integration of kinetic ordinary differential equations were applied. Sufficient accuracy of the method used is the prerequisite for converging of the algorithm which has to minimize the sum of deviation squares. Our program "TA-kin" enables effective evaluations because of its high flexibility.

*Keywords*: Thermokinetics; Kinetic parameters; Non-linear optimization; Software; Calcium oxalate monohydrate

## 1. Introduction

By increasing experimental accuracy of thermal analysis, such as DSC and TG, as well as adiabatic and isoperibolic calorimetry, kinetic evaluation becomes more and more the possible. The temporal course of the quantity to be measured is a sufficient basis for the determination of the kinetic of chemical reactions.

The degree of conversion, or in the case of DSC measurements the rate of conversion, can be calculated directly from experimental data for simple reactions as well as for some complex reactions. This information leads to the differential or the integrative determination of kinetic parameters.

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The differential method requires knowledge of the time dependence of reaction rate or rate of conversion, respectively, which has to be computed by application of numerical differentiation procedures in most cases. Note that scattering data require a smoothing procedure before applying a numerical differentiation.

Integrative kinetic evaluations demand the solution of the differential rate law based on the presumed reaction model. Using the Arrhenius equation for the temperature dependence of the rate constant $k$, a complete analytical solution of the ordinary differential equation is not possible. Therefore, numerical procedures have to be introduced.

Kinetic parameters like the frequency factor $k_0$, activation energy $E_A$ and partial orders $n_i$ of a reaction are of non-linear character in the reaction law

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_0 \exp(-E_A / RT) f(x), \quad x = \Delta c_i / \nu_i \tag{1}$$

The kinetic function $f(x)$ given below is an example for a second order reaction:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(c_{0,A} - x)^{n_1} (c_{0,B} - x)^{n_2} \tag{2}$$

In the 1970s and 1980s, linearization of the TA curves was generally desired. Corresponding mathematical transformations and approximation formulas realized it to permit analytical determination of the activation parameters.

Due to the fast development of computer performance, time economized non-linear optimizations are available with high precision nowadays. The consequent introduction of modern computers in thermoanalytical laboratories has resulted in an increasing variety of possibilities for the application of non-linear evaluation procedures. Their introduction in thermal analysis has been in place in Germany (Greifswald and Jena) since the end of the 1980s.

The commercial software RATE (*engl./amer.*) and KINETICS MK (St. Petersburg) and the program TA-kin, developed in Greifswald, are actually used for the evaluation of an international ring experiment. The main part of the three programs is a non-linear regression, i.e. an iteratively working algorithm for minimization of the sum of deviation squares (SDS) relative to the kinetic parameters. In the case of an integrative evaluation, the reaction model, consisting of the basic differential rate laws, must be integrated for each step of the iteration to obtain the corresponding values for the calculation of the SDS function. The coupling with an algorithm, minimizing functions, is therefore also named the estimation of parameters in ordinary differential equations.

In the following, the possibilities and the applied numerical procedures of the programs mentioned above are characterized.

## 2. Software

The computer application TA-kin was essentially developed in the main parts by V. Tiller [1] using Borlands Turbo Pascal. Some characteristics of the programs are listed.

TA-Kin:

- input of measured data by import of ASCII files,
- numerical integration of ordinary differential equations: adaptive Runge-Kutta procedures of fourth and fifth order [2], BDF routine according to Gear [3],
- simulation of the presumed model of reaction, data output as an ASCII file and graphics output as an HPGL file,
- graphical presentation of measured data and simulation data,
- least squares method according to Levenberg and Marquardt, output of results as an ASCII file.

The program RATE [4] is one component of the software package BatchCAD. It enables the user to evaluate reactions in the liquid and possibly also in the gaseous phase using calorimetric data and concentration data from experiments carried out in batch, semi-batch or continuous mode.

KINETICS MK [5] assists particularly the evaluation of TG and DSC data as well as of batch experiments. Characteristics of both programs are given below.

- input of measured data by keyboard or by import of ASCII files,
- definition of reaction models with an optional combination of simultaneous reactions, consecutive reactions, reversible and autocatalytic reactions,
- numerical integration of ordinary differential equations: BatchCAD, adaptive Runge-Kutta procedure of fourth order, Burlish-Stoer; KINETICS MK, fourth order Runge-Kutta routine, BDF routine according to Gear,
- graphical presentation of model simulation on the display,
- least squares methods; BatchCAD, simplex algorithm; KINETICS MK, modified Gauss-Newton procedure, output of results as ASCII file.

## 3. Special aspects of integration of ordinary differential equations (ODEs)

Optimization of kinetic parameters in the differential rate law requires the calculation of function values, e.g. conversion variables, by integration of the reaction model containing one or more ODEs.

Sufficient accuracy of the applied integration method has to be realized to guarantee the safety of the algorithm minimizing the sum of deviation squares.

Runge-Kutta methods with implementation of adaptive control of stepsize have been used [2]. With fourth order Runge-Kutta, the most straightforward technique is step doubling. Each step is taken twice, once as a full step, then, independently, as two half steps. The difference between the two numerical estimates $y_h(x + h)$ and $y_{h/2}(x + h)$ is a convenient indicator of truncation error. The comparison of the absolute or the relative error with a chosen accuracy $\varepsilon_{\max}$ gives information on how to increase (step succeeded) or to decrease (step failed) the stepsize $h$. Runge-Kutta with adaptive stepsize control is a very suitable method if the right-hand side of the ODE involves a function which is evaluated by table look-up and interpolation. In these cases Runge-Kutta should be preferred to backward differentiation formula (BDF) methods and the Burlish-Stoer procedure.

With Burlish-Stoer, one may obtain highly accurate solutions of ODEs with low computational effort. One interval $(x,x + h)$ will be integrated with different stepsizes and the

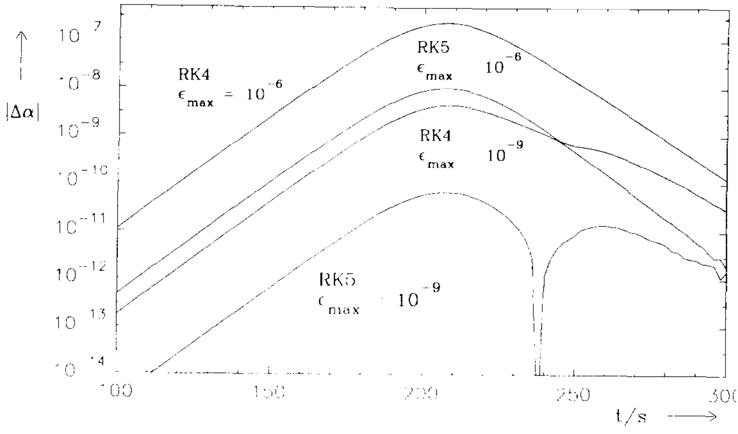

Fig. 1. Absolute difference between the analytic and numeric integration of the rate law of an isothermal autocatalytic reaction; adaptive Runge-Kutta fourth order (RK4) and fifth order (RK5) were applied with the accuracy values $\varepsilon_{max} = 10^{-6}$ and $10^{-9}$, respectively.

function value $y(x+h)$ is obtained by extrapolation to an infinitesimal stepsize. BDF routines use for the calculation of a function value $y(x)$, the already computed values and the approximation of its first derivative $y'(x)$. These methods should be favoured if the reaction model contains a stiff set of ODEs.

Fig. 1 demonstrates the accuracy of two adaptive Runge-Kutta routines. A simple autocatalytic reaction $A + B \rightarrow 2B + \cdots$ was chosen and isothermal conditions were assumed. Therefore analytical solution of the rate law given below, is possible.

$$\frac{dx}{dt} = k(c_{0,A} - x)(c_{0,B} + x) \tag{3}$$

With the rate constant $k = 1$ (mol $l^{-1})^{-1}$ $s^{-1}$, initial concentrations $c_{0,A} = 0.1$ mol $l^{-1}$ and $c_{0,B} = 10^{-10}$ mol $l^{-1}$ the maximal reaction rate is reached after about 200 s. The absolute difference between the analytical and the numerical solution for the degree of conversion ($\alpha = \Delta c_i / c_{i,0}$) is plotted versus time.

The relative operation accuracy $\varepsilon_{max}$ of the adaptive Runge-Kutta integrator in the test shall be $10^{-6}$ and $10^{-9}$, respectively. It should be mentioned that higher order routines of Runge-Kutta do not guarantee results of higher accuracy automatically. Integration operations using a fixed stepsize waste computational time in most cases. The induction time of the reaction model equals 150 s. In the second time range (150–250 s in Fig. 1) the reaction rate increases rapidly and smaller stepsizes are a prerequisite to obtain acceptable results. On the other hand, the induction phase may be integrated by larger steps. The solution of such problems leads to the application of adaptive integration routines. To learn first information about the course of the reaction, one should choose a relatively large stepsize $h$ and accuracy value $\varepsilon_{max}$, respectively.

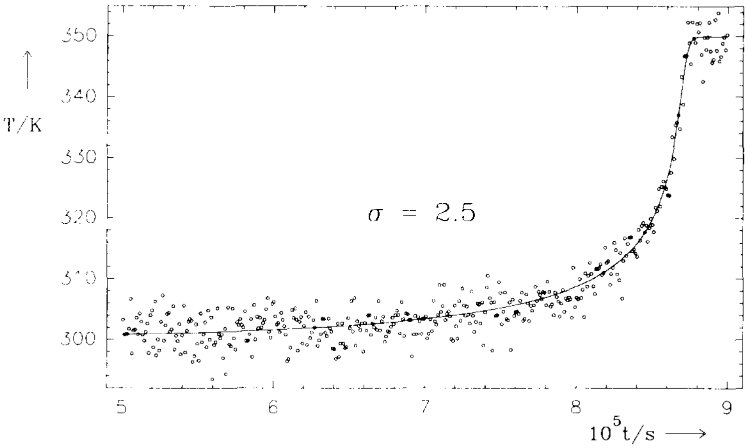

Fig. 2. Simulation of an autocatalytic reaction with the activation parameters $\ln(k_0/(\text{mol l}^{-1})^{-1}\text{ s}^{-1}) = 20$ and $E_A = 80$ kJ mol$^{-1}$, the initial concentrations $c_{0,A} = 1$ mol l$^{-1}$ and $c_{0,B} = 10^{-3}$ mol l$^{-1}$, the final temperature difference $\Delta T = 50$ K (defined by heat capacity of the reaction mixture and enthalpy of reaction); adding regular distributed errors to the simulation data gives the discrete data points.

## 4. Methods for the minimization of the sum of deviation squares

Gauss' method of least squares is successfully applicable in nature science because of its relationship to measuring errors of regular distribution.

$$\text{SDS} = \sum (y_{i,\text{calculated}} - y_{i,\text{observed}})^2 \tag{4}$$

model functions: explicit $y = f(x, p_i)$ or ODEs $y' = f(x, y, p_i)$.

Table 1

Estimation of activation parameters in the rate law of an autocatalytic reaction by application of three programs based on the least squares method

| Standard deviation σ | TA-kin (Greifswald) Levenberg-Marquardt | | RATE (BatchCAD) Simplex | | Kinetics-MK (Russian Scientific Center) Modified Gauss-Newton | |
|---|---|---|---|---|---|---|
| | $\ln[k_0/\text{s}^{-1}$ (mol l$^{-1})^{-1}]$ | $E_A$/kJ mol$^{-1}$ | $\ln[k_0/\text{s}^{-1}$ (mol l$^{-1})^{-1}]$ | $E_A$/kJ mol$^{-1}$ | $\ln[k_0/\text{s}^{-1}$ (mol l$^{-1})^{-1}]$ | $E_A$/kJ mol$^{-1}$ |
| 0.05 | 20.00 | 80.00 | 20.02 | 80.05 | 20.06 | 80.13 |
| 0.5 | 19.95 | 79.87 | 20.08 | 80.21 | 21.35 | 83.39 |
| 1.0 | 20.05 | 80.14 | 19.93 | 79.84 | 21.34 | 83.48 |
| 2.5 | 19.74 | 79.36 | 20.72 | 81.80 | 20.26 | 81.30 |

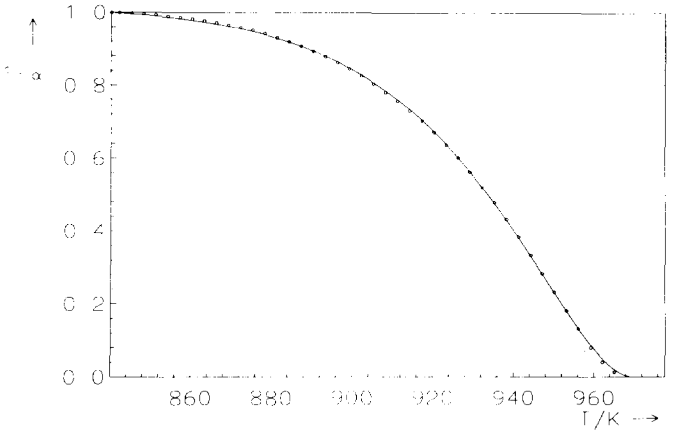

Fig. 3. TG measurement of the decomposition of $CaC_2O_4 \cdot H_2O$ in argon; third stage of the reaction (split gas $CO_2$); assuming the reaction order $n = 1/2$, estimated activation parameters: $\ln(k_0/s^{-1}) = 22.3$, $E_A = 235$ kJ mol$^{-1}$; the measured data are plotted by circles.

Non-linear regression is an iterative procedure to find out the minimum of the SDS-function. Often that procedure is called optimization or fitting. By varying the model parameters $p_i$ the algorithm has to realize a decrease of the SDS function during each iteration until a minimum is reached. Note that iterative procedures cannot guarantee to find the global minimum in each case. Several sets of start values may result in different local minima instead of the global one. Algorithms for minimization of the sum of deviation squares differ from each other in determining a local deepest descent of SDS-function.

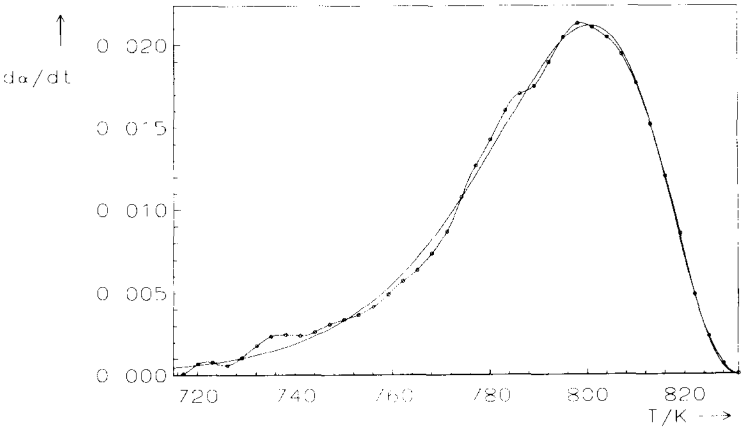

Fig. 4. DSC measurement, decomposition of $CaC_2O_4 \cdot H_2O$ in a mixture of air and argon; second stage of reaction (split gas CO); assuming a first order reaction, estimated parameters: $\ln(k_0/s^{-1}) = 33.5$, $E_A = 263$ kJ mol$^{-1}$, $n = 0.80$; the measured curve is plotted by circles.

Simple autocatalysis under adiabatic conditions was used to test optimization methods. For that purpose regular distributed errors of a fixed standard deviation were superposed on simulated temperature–time curves. The rate law is formulated as in Eq. (3) with application of the Arrhenius relation.

The conversion variable $x$ is directly proportional to the absolute difference of temperature $\Delta T(t) = |T(t) - T(0)|$. The simulated temperature–time curve and a data set with a certain distribution of errors is shown in Fig. 2. Results of optimization are given in Table 1. Note that for the standard deviation $\sigma = 2.5$, i.e. a third of the data points is outside the interval limit of $T - 2.5$ K and $T + 2.5$ K, all three methods converge. Because of the high correlation of the Arrhenius parameters [6] their drift increases if experimental data are charged by systematic errors.

Applications of non-linear regression to explicit functions and ODEs [7,8] were realized with a lot of TG and DSC data, which are part of the international ring experiment *Thermal Decomposition of Calcium Oxalate-Monohydrate* by the workgroup Kinetics in the German Society for Thermal Analysis (GEFTA). At first the different formats of data files from 12 laboratories participating in this ring experiment were converted to a standard format. That enabled efficient operation of kinetic evaluations and the direct graphic comparison of different sets of data.

Figs. 3 and 4 demonstrate evaluations of a TG and a DSC analysis. A final report about the kinetic results of the ring experiment will be given in September at the Eleventh Conference of the GEFTA in Sopron/Hungary.

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