# EFFECTIVE SEARCH OF STARTING VALUES FOR KINETIC PARAMETERS ESTIMATION

*H. L. Anderson, R. Strey, A. Kemmler and D. Haberland*

University of Greifswald, Institute of Physical Chemistry, Soldmannstr. 23,
D-17489 Greifswald, Germany

## Abstract

For the calculation of kinetic parameters from thermal data files numeric optimization has been well introduced. But suitable starting values near the global minimum of the sum of deviation squares are needed for a successfully parameter estimation. Namely the search for starting values requires a lot of time and diminishes the effectiveness of the total procedure. Therefore we have developed an algorithm of the automatic search of starting values for the optimization of activation energy end frequency factor of a chemical reaction.

This search procedure uses the knowledge of the specific course of the corresponding *SDS* surface in the near of its global minimum. In this area the *SDS* describes two plateaus separated by a narrow valley. The search procedure avoids starting values at one of these plateaus. This PC program is part of the complex software package TA-kin v3.3 for kinetic evaluation of thermal measurements.

**Keywords:** activation energy, compensation effect, kinetic analysis, non-linear optimization, starting values

## Introduction

For the estimation of kinetic parameters from thermal data files numeric optimization more and more increases to the method of the first choice [1–3]. These methods are founded on the numeric integration of the kinetic rate equation. Therefore known integration methods of Runge-Kutta type can be used. The comparison of simulated curves and measured data files is an expression of the quality of fitting. An usual basis of comparison is to calculate the sum of deviation squares (*SDS*). The *SDS* yields of the measured data $y_i$ and the simulated curve $h(x_i, a, b,...)$ obtained by the numeric integration of the reaction model.

$$SDS(a, b,...) = \sum_{i=1}^{n} (y_i - h(x_i, a, b,...))^2 W_i \tag{1}$$

In this procedure weight factors $W_i$ are used frequently, which are mainly obtained from experiences. This factors should characterize the different effectiveness of each data set to the total evaluation. The parameters $a, b,...$, for example activation energy or frequency factor, of the kinetic model, will be changed by suitable
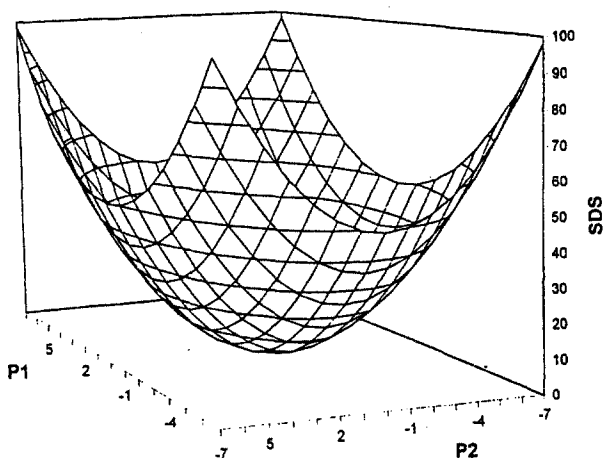
**Fig. 1** Shows an idealized function $Z(x,y)$, whose minimum can be found easily by a numeric optimization method from any starting point. Such ideal cases hardly arises in the chemical kinetic

variation to bring the measured curve $y$ into line with the simulated curve $h(a,b,...)$. The best fit are obtained if $SDS(a,b,...)$ has reached its global minimum. Mostly this minimization will be done by the Marquardt-Levenberg algorithm [4], which allows a fast determination of the kinetic parameters.

But such numeric methods need suitable starting values near global minimum, if the $SDS$ function has not an ideal shape like that of Fig. 1. If there are not only one global minimum but also local minimums the destinated values of the mini.mization depends decisively on the chosen starting values. Starting firom adverse initial values the optimization can stop at a local minimum or diverge. Minimization procedures which require the gradient for the searching beam as given by Newton or Marquardt-Levenberg [5], fail completely if the $SDS$ is constant near the starting point. This can happened in the real case of Fig. 2. That's why the search of suitable starting values is the basis for the success of the numeric minimization.

It is possible to use a special minimization method for the search of starting values which considers additional information about the specific problem which make it easier to find the global minimum. If the basic shucture of the $SDS$-surface is known for a given optimization problem then the starting values can be found by mapping an selected parameter area with use of the knowledge about the typical course of the $SDS$ in the surroundings of its minimum.

In the following such an algorithm will be given for the estimation of starting parameters of the joint optimization of activation energy $E_A$ and frequency factor $\ln k_0$ of a chemical reaction. Calculating the sum of deviation squares in selected areas of $E_A$ and $\ln k_0$ a surface will be obtained, which is characterized mainly by two plateaus of different levels as shown in Fig. 2. These areas of almost constant $SDS$ values are separated by a narrow ditch with steep descent. This "banana valley" defines the global minimum, so it slopes slight upward in both directions within the trench.
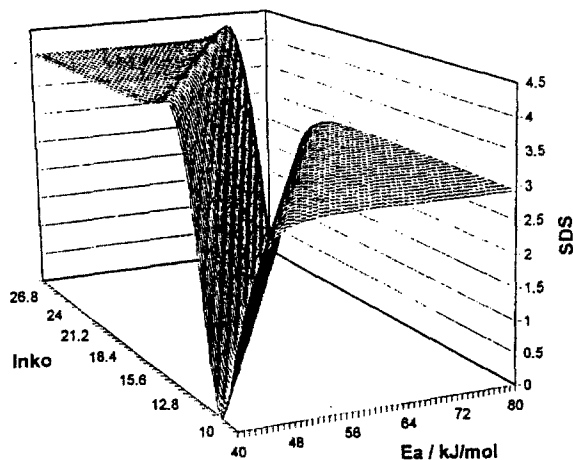
**Fig. 2** Shows the typical course of the *SDS* over an interval of $E_A$ and $\ln k_0$ for a reaction of first order under isoperibol conditions. The original parameters are $E_{Ao} = 60$ kJ mol$^{-1}$ and $\ln k_{oo} = 20$. In the areas of very high and very slow conversion speed the *SDS* is nearly constant. ($c_R = 150$ J K$^{-1}$, $K = 0.25$ W K$^{-1}$, $T_{env.} = 273.15$ K, $V_{reactor} = 40$ ml, $C_0 = 1.0$ mol l$^{-1}$, $T_0 = 273.15$ K, $\Delta_R H = -50$ kJ mol$^{-1}$, time of reaction: 3600 s, number of points: 100)

The projection of the valley bottom to the plane of parameters follows a straight line which causes the so called "compensation effect" [6]:

$$\log k_0 = b + a\,\frac{E_A}{R} \tag{2}$$

Varying the kinetic parameters along this line the *SDS* value changes only very small. Therefore the experimental curve can be described by different kinetic parameter sets within the accuracy limit of measurement. Thus, only k has the correct value, but not $k_0$ and $E_A$. Such a compensation form has exclusively mathematical reasons and does not transform any physical chemical expression. In the special case of Fig. 2 a rampart is situated between the searched valley and the left plateau. Starting on it a global minimum cannot be found. For an effective search the starting point must be defined within the banana valley.

## Method of mapping

The search for suitable starting values is directly derived from the geometrical discussion of Fig. 2. At first the *SDS* in a reasonable expectable area of $E_A$ and $\ln k_0$ will be scanned using a Monte-Carlo method [7]. Therefore the *SDS* values at random coordinates within their two-dimensional parameter room will be calculated and sorted into groups. The ordering of the *SDS* values will be done by their amounts. A *SDS* value belongs to a cluster if its difference to the average of all values within the cluster is less then a stipulated maximum distance ε. For a successful

procedure it is favorable to chose an ε of one percent of the *SDS* value at maximum conversion speed. If there is not a suited clusters, a new one must be created. The calculation and classification of new values reiterate until a braking off condition will be reached. Possible braking off conditions are the exceeding of a stipulated maximal number of points, of clusters, of points within a cluster and the decision of the user respectively. These conditions can be combined to a global braking off condition.

## Evaluation of the mapping

After mapping, the clusters will be classified according to their amount of containing points. Then the shortest connection between two points from the both largest clusters will be determined. Along this straight line the starting values will be found by an one dimensional minimization. Therefore a modified halfening algorithm can be used, considering the special course of the *SDS*. Namely the shortening of the interval must lead to a new interval with different value at the end and the beginning. So the interval includes points of the valley after every iteration step. The destination point of this minimization can be the starting point of the nonlinear optimization if its *SDS* amount is smaller than all calculated by Monte-Carlo. Otherwise the point with the smallest *SDS* value will be defined as starting point.

This procedure has been included in our program package TA-kin v3.3 [8, 9] which has been developed for the kinetic analysis of DSC, TG, DTA and calorimetric experiments. For practical measured curves of the thermal analysis we could show that the expenditure of time can decreases rapidly by using the automatic
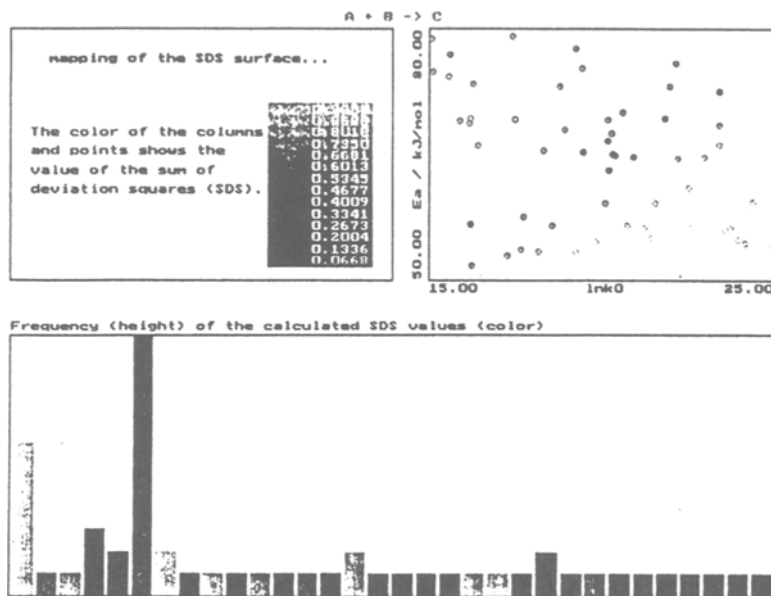


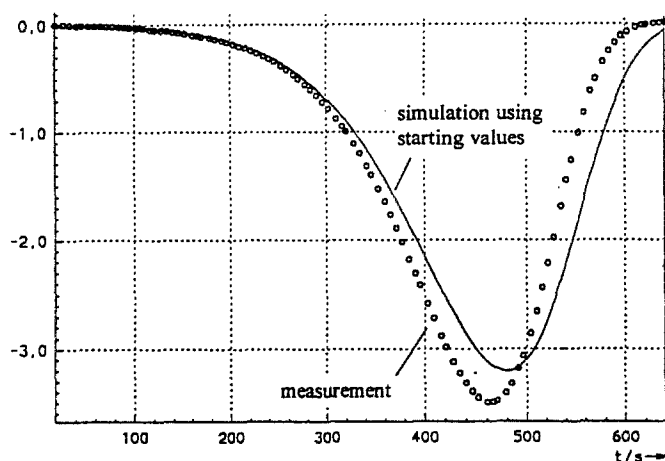Fig. 3 Shows a screen shot of the Monte-Carlo step of this procedure

**Fig. 4** Shows a measured DSC-curve of a *cis-trans* conversion of azobenzene and the corresponding simulation on the basis of kinetic parameters found by our procedure. Using this starting values the exact parameters can be found by a Marquardt-Levenberg algorithm in only three steps

search for starting values. Figure 3 shows a screen shot of the application of TA-kin v3.3 during the search for starting values of the chemical reaction of phenyl isocyanate with alcohol. The mapping of the *SDS* over the chosen area of parameters as well as the frequency of *SDS* values are shown. Another application of this procedure is shown in Fig. 4. A starting point for the evaluation of a DSC-measurement of *cis-trans* conversion of azobenzen in melted state was generated. This starting values lead to a simulated curve close to the course of the experimental data. Starting from this parameter set the exact values can be found within four seconds with three steps using a Marquardt-Levenberg algorithm.

Now it is possible to carry out a high automatic evaluation of TA curves without many operations of the user. To this there are successes for DSC, TG and calorimetry.

## References

1 H. Anderson, Thermochim. Acta, 203 (1992) 515.
2 H.Anderson and J. Mentel, J. Thermal Anal., 41 (1994) 471.
3 H. L.Anderson, A. Kemmler and R. Strey, Thermochim. Acta, 271 (1996) 23.
4 D. W. Marquardt, J. Soc. Indust. Appl. Math., 11 (1963) 431.
5 P. Kosmol, "Methoden zur numerischen Behandlung nichtlinearer Gleichungen und Optimierungsaufgaben", 2. Aufl., Teubner Stuttgard 1993.
6 N. Eisenreich, J. Thermal Anal., 19 (1980) 289.
7 I. N. Bronstein and K. A. Semendjajew, "Taschenbuch der Mathematik", 5. Aufl., Teubner Leipzig 1988, S.E207.
8 H. L. Anderson, A. Kemmler, K. Heldt and R. Strey, J. Thermal Anal., 47 (1996) 543.
9 H. L. Anderson, A. Kemmler and R. Strey, Thermochim. Acta, 271 (1996) 23.