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In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

ADIABATIC DECOMPOSITION KINETICS BY NON-LINEAR OPTIMIZATION

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Abstract

Reactions with large negative enthalpy changes are often encountered in the chemical industry. Sometimes they give rise to technical dangers and hazards, including explosions. This investigation concentrates on examination of adiabatic temperature-time-curves and gives non-linear optimization procedures for obtaining kinetic parameters of simple decompositions, e.g. *o*-nitrobenzaldehyde, two types of autocatalysis, consecutive reactions and competitive consecutive reactions. The advantage of this computing method is that only differential kinetic equations are needed.

Keywords: adiabatic decomposition, explosions, kinetics, non-linear optimization, organic compounds, software

Introduction

Reactions with relatively large changes of enthalpy often have very important industrial applications. Sometimes, however, they give rise to technical risks and dangers in chemical laboratories and plants. In the past fifteen years, chemical technology has, with increasing success, striven for better practical control and for improved theoretical precalculation of the behaviour of the reaction mixture under defined conditions [1–4]. This special kind of thermal analysis principally considers explosions caused by total accumulation of the reaction heat. Such hazardous events have been described by Hub [5] and Hakl [6].

Grewer [7] and Hugo [8] used different ways to solve this problem and obtained valuable results. In particular, there are three different conditions which have been thoroughly investigated. First, the observation of the reaction mixture under adiabatic conditions, with defined initial temperature T_i. After some time,

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which may be minutes, hours or days, the temperature increase becomes faster and faster due to accumulation of the reaction heat and simultaneous acceleration of the reaction rate. The temperature increases to a final temperature T_f. This gives a temperature change of ΔT_f. There is little risk as long as the value of ΔT_f is not greater than 100 K.

Second, in the so-called batch technique, after the last reaction component has been added, the heat can only partially leave the reactor. Depending on the value of the heat exchange coefficient i.e., the efficiency of cooling, danger may or may not arise. In the third case, the last component is introduced continuously over a preset time interval. In this semi-batch technique [9], it may be easier to guarantee safety while the reaction is progressing. Examples from chemical industry demonstrated that his technique is also not without risk, e.g., if the stirrer fails [8].

Our report will concentrate on the results obtained for the first case, i.e., an adiabatic decomposition reaction in fluid or in solid systems. Unstable substances are stored at the initial temperature T_i without any heat transfer to the environment. Therefore ΔT_f will reach the value of $\Delta H/C_p$ at the conclusion of reaction. For a number of reactions this ΔT_f may cause hazards. The time at which the temperature-time-curve has an inflection point is called the induction time τ. For many of the dangerous decompositions the induction time is indistinguishable from the final time, i.e., the time of last heat production. Figure 1 shows T-t-curves of such a kind. These investigations are effectively supplemented by DTA/DSC-measurements. Since the techniques of calorimetry, as well as those of DTA/DSC, have now become precision methods, their theoretical basis is important. We show here that a unified procedure for these three measuring techniques is possible, if some prerequisites are known and non-linear methods of mathematics are applied [10–13].

Up to now the controversies between DTA and calorimetric ΔT-t curves have entailed the use of correction terms. But it is not necessary in all reactions to define an autocatalytic effect. Although, in several cases, autocatalysis has to be included (see Grewer [1]), a new kinetic evaluation using basic differential equations (DE) and non-linear optimization (NLO) will show which reaction model is consistent with the equations of formal kinetics.

Our investigation concentrates on adiabatic T-t-curves and their kinetic explanation. Experimental curves [1] and computer-simulated curves of the following types are used:

- simple decompositions
- consecutive reactions
- competitive consecutive reactions, both with and without the influence of autocatalysis.

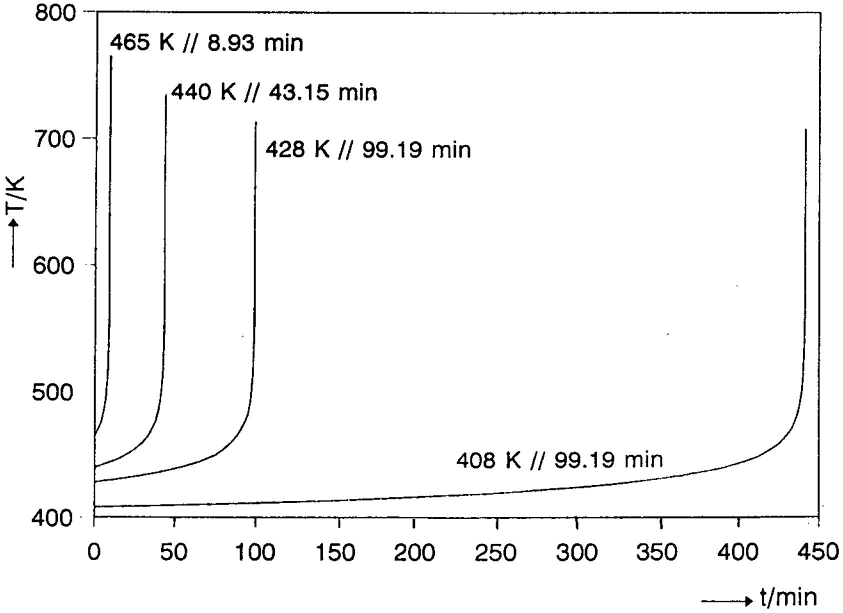

Fig. 1 Decomposition of *o*-nitrobenzaldehyde under adiabatic conditions $E = 116\ \mathrm{kJ{\cdot}mol^{-1}}$, $\ln(k_o\ \mathrm{min}) = 24.993$, $\Delta T_f = 300$ K

Results

Simple decompositions

These will follow the differential description of reaction rate as given in Eq. (1). If adiabatic conditions are guaranteed then Eq. (2) and Eq. (3) are also valid.

$$\frac{dx}{dt} = k_o \exp\left(-\frac{E}{RT}\right)(1-x)^n \qquad (1)$$

$$T = T_i - \frac{Q}{C_p}x \qquad (2)$$

$$\frac{dx}{dt} = k_o \exp\left(\frac{-E}{R(T_i + x\Delta T_f)}\right)(1-x)^n \qquad (3)$$

where

x = extent of reaction
T_i = initial temperature

$\Delta T_f = -Q/C_p = T_f - T_i$
Q = reaction heat (kJ/mol)
k_o = frequency factor
E = activation energy (kJ/mol)
n = reaction order
C_p = heat capacity (J/K)

The differential equations DE were used to simulate the x-t and the T-t-curves and their dependence on activation energy and frequency factor.

If the adiabatic T-t-curve is known, then we can determine x with the help of Eq. (2). From these values of x, the kinetic parameters E, k_o and n can be directly fitted to Eq. (3) by non-linear methods. A program for parameter fitting of ordinary differential equations was used [10]. This program was developed from a combination of the 'trust-region-method' [11] and the routine after Marquardt. The advantage of the direct estimation of the kinetic parameters is that the parameters are valid under isothermal as well as under non-isothermal conditions, e.g. TG, DTA, DSC, because the usual methods of approximation were avoided [12, 13]. As for any non-linear optimization, values for the parameters to be determined have to be estimated before computation starts.

From Grewer [1, Fig. 13] we obtained experimental curves for the adiabatic decomposition of o-nitrobenzaldehyde, for four initial temperature T_i, and values of the heat of reaction and the activation energy, which were obtained from the $\ln\tau - 1/T$-diagram (k_o remained unknown).

The assumption of a first order reaction is suitable for the determination of k_o in Eq. (4).

$$\frac{dx}{dt} = \exp\left(\frac{-E}{R(T_i + x\Delta T_f)} + \ln k_o\right)(1-x) \tag{4}$$

If the value of ΔT_f is assumed to be 300 K, then a simulation of the T-t-curve, starting at T_i = 423 K, and direct parameter fitting to the T-t-data lead to an $\ln k_o$ (min^{-1}) value of about 25.45. The complete set of parameters obtained in this

Table 1 The dependence of the induction time /min on the activation energy, E / kJ·mol^{-1} and initial temperature, T_i / K for $\ln k_o$ (min^{-1}) = 24.99 and ΔT_f=300 K

T_i / K	Experim. (1)	E = 115	E = 116	E = 117
408	406	332	441	550
428	99.2	75.7	99.19	131
440	59	33.5	43.15	57
465	11	6.96	8.93	11.5

way allows the immediate plot of the curves investigated (Fig. 1). The agreement with the original Grewer-curves [1, Fig. 13] is satisfactory. Taking this into account, it seems to be unnecessary to describe the decomposition of *o*-nitrobenzaldehyde as an autocatalytic mechanism. Table 1 shows the sensitivity of our fitting.

Simple decompositions including autocatalysis

Several authors introduce an autocatalytic term into their considerations of hazardous decompositions. To prove the influence of an autocatalytic effect on the adiabatic *T*-*t*-curve, we started from the basic DE. Eq. (5) and Eq. (6) define the two reaction schemes.

$$\mathrm{A} \rightarrow \mathrm{B}; \quad \mathrm{A} + \mathrm{B} \rightarrow 2\mathrm{B} \tag{5}$$

$$\mathrm{A} + \mathrm{B_i} \rightarrow \mathrm{B} + \ldots\ldots \tag{6}$$

Type I:

$$\frac{\mathrm{d}x_1}{\mathrm{d}t} = \exp\left(\frac{-E}{R(T_\mathrm{i} + x_1\Delta T_\mathrm{f1} + x_2\Delta T_\mathrm{f2})} + \ln k_\mathrm{o1}\right)(1 - x_1 - x_2) \tag{7}$$

$$\frac{\mathrm{d}x_2}{\mathrm{d}t} = \exp\left(\frac{-E}{R(T_\mathrm{i} + x_1\Delta T_\mathrm{f1} + x_2\Delta T_\mathrm{f2})} + \ln k_\mathrm{o2}\right)(1 - x_1 - x_2)(x_1 + x_2)$$

with

$$\Delta T_\mathrm{f1} = -\frac{Q_1}{C_\mathrm{p}}$$

and

$$\Delta T_\mathrm{f2} = -\frac{Q_2}{C_\mathrm{p}}$$

Type II:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \exp\left(\frac{-E}{R(T_\mathrm{i} + x\Delta T_\mathrm{f})} + \ln k_\mathrm{o}\right)(1 - x)(B_\mathrm{i} + x) \tag{8}$$

According to these chemical descriptions, we obtain the DE Eq. (7) and Eq. (8), where B_i represents the initial concentration of the catalyst. Because the rate controlling reaction is of second order, both cases of autocatalysis are comparable. For type I, no catalyst is needed at the starting point, in contrast to type II, where the induction time is strongly dependent on the initial concentration of the catalyst.

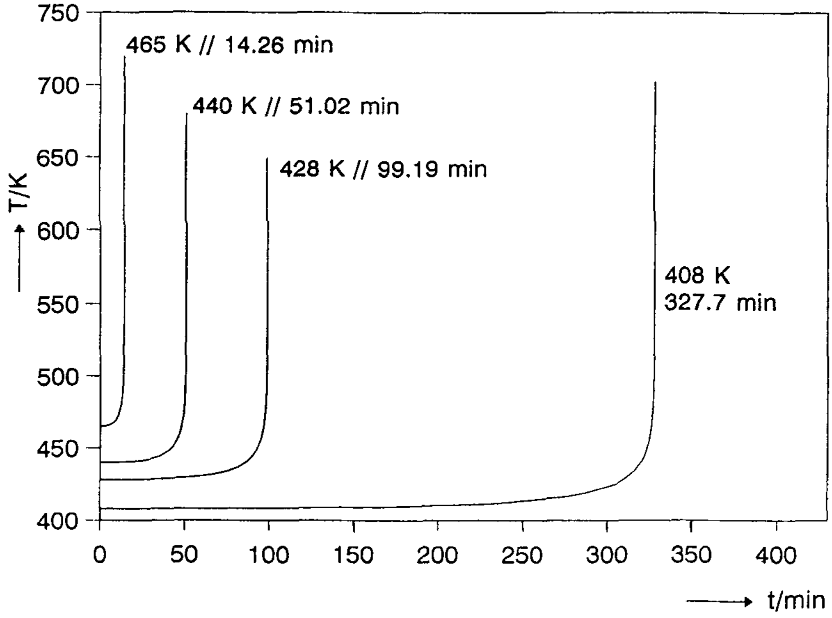

Fig. 2 Autocatalysis of decomposition of *o*-nitrobenzaldehyde as hypothesis $\Delta T_{f1} = 30$ K, $\Delta T_{f2} = 300$ K, $E_1 = 106$ kJ·mol^{-1}, $E_2 = 83$ kJ·mol^{-1} $\ln(k_{o1}$ min$) = 19.962$, $\ln(k_{o2}$ min·mol$) = 19.962$

In Figs 2 and 3, the simulation of the *o*-nitrobenzaldehyde decomposition under catalytic conditions is shown. Comparison with Fig. 1 demonstrates the distinct deviation from the basic experimental curve. In contrast to Fig. 1, both types of autocatalysis result in *T*-*t*-curves with long horizontal periods, clearly shown for type II. Then, in the vicinity of the induction time, the slope increases very rapidly. This behaviour differs markedly from the experimental curves for the decomposition, which are very similar to the set of curves in Fig. 1. It does not matter whether the first reaction in Eq. (5) is exothermic or endothermic, as long as the reaction enthalpy is distinctly lower than that of the second reaction. The induction time is shifted only by a few minutes.

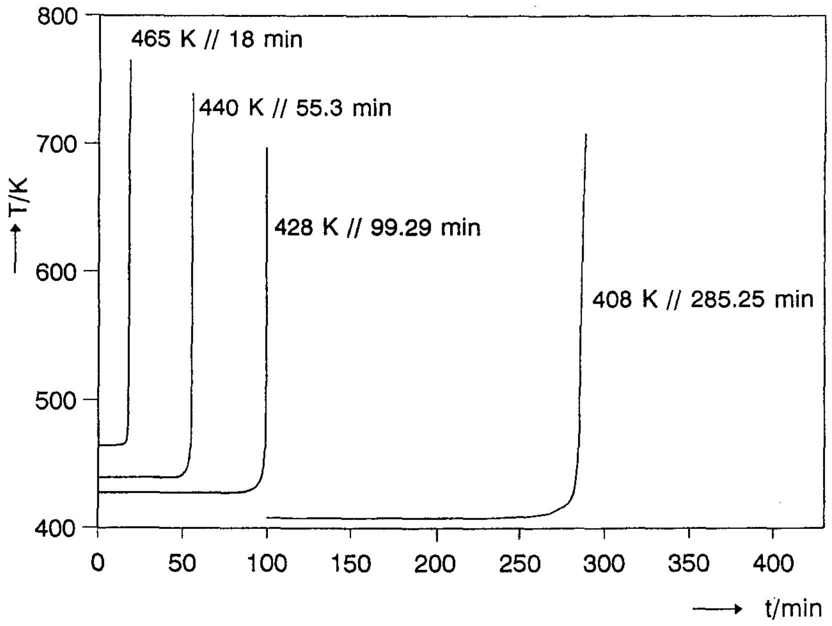

Fig. 3 Autocatalysis of decomposition of *o*-nitrobenzaldehyde as hypothesis $\Delta T_f = 300$ K, $E = 77$ kJ·mol^{-1}, $\ln(k_o$ min·mol$) = 20.028$, $B_i = 1E{-}10$ mol/l

It should be emphasized, that the simulation of the autocatalytic reactions requires very high accuracy for the numerical integration of the DE, and small stepwidths are needed in the starting region.

Parameter fitting

To estimate the efficiency of evaluation of kinetic parameters by direct data fitting according to Eq. (3) and Eq. (4) or (8), two sources of data have been used: experimental curves from Grewer [1] and simulated curves with different standard deviations of scattering of random errors. It can be shown that the determination of the frequency factor and the reaction order offers no problems if the activation energy is obtained beforehand e.g. from the $\ln\tau - 1/T$-diagram. The estimated values may deviate strongly from the exact values after optimization and difficulties with convergence are rare. In the normal region of optimization, a free choice of all kinetic parameters (without knowledge of E) is possible, i.e., free fitting of E, $\ln k_o$ and n on the basis of an accurate T-t-curve. The prerequisite remains that the scattering of data should not be high and, in the case of autocatalysis, the curvature should not be too large. The method becomes unstable in regions of rapid temperature increase.

In several cases, it is appropriate to preset the reaction order, so that the region of convergency increases. As a rule, this means low experimental scattering (SD 0.003). The starting values of E and $\ln k_o$ may deviate by as much as 10% from the accurate values. For easier optimization, the starting values should be lower than the expected accurate ones. To search for the starting values, simulations at varying E and $\ln k_o$ values should be used.

If the exothermic reaction enthalpy is large (resulting in $\Delta T_f > 1000$ K), fitting problems arise. It is thus an advantage, in the case of autocatalysis, if the reaction enthalpy has relatively low values so that $\Delta T_f < 100$ K.

Consecutive reactions

The following types of reaction were the basis for simulations

$$A + B \xrightarrow{k_1} C + \ldots\ldots \tag{9}$$

$$C \xrightarrow{k_2} E + \ldots\ldots \tag{10}$$

$$\frac{dx_1}{dt} = \exp\left(\frac{-E}{R(T_i + x_1\Delta T_{f1} + x_2\Delta T_{f2})} + \ln k_{o1}\right)(1 - x_1)^2 \tag{11a}$$

$$\frac{dx_2}{dt} = \exp\left(\frac{-E}{R(T_i + x_1\Delta T_{f1} + x_2\Delta T_{f2})} + \ln k_{o2}\right)(x_1 - x_2) \tag{11b}$$

If under adiabatic conditions, the rate constants k_1 and k_2 are of similar magnitude, then the DE Eq. (11a+b) can be used for the simulation of T-t-curves and their dependence on the kinetic parameters, but it is impossible to separate x_1 and x_2 on the basis of experimental adiabatic T-t-data. For this general case, parameter determination by direct fitting is impossible.

The two extreme cases, Eqs (12a) and (12b) are of special interest.

$$k_2 >> k_1 \tag{12a}$$

$$k_2 << k_1 \tag{12b}$$

Under the conditions of Eq. (12a), the values of the variables x_1 and x_2 converge after a certain time interval. This is equivalent to a reduction of the two DE Eqs (12) to one DE. Then a direct fitting of T-t-data by non-linear optimization

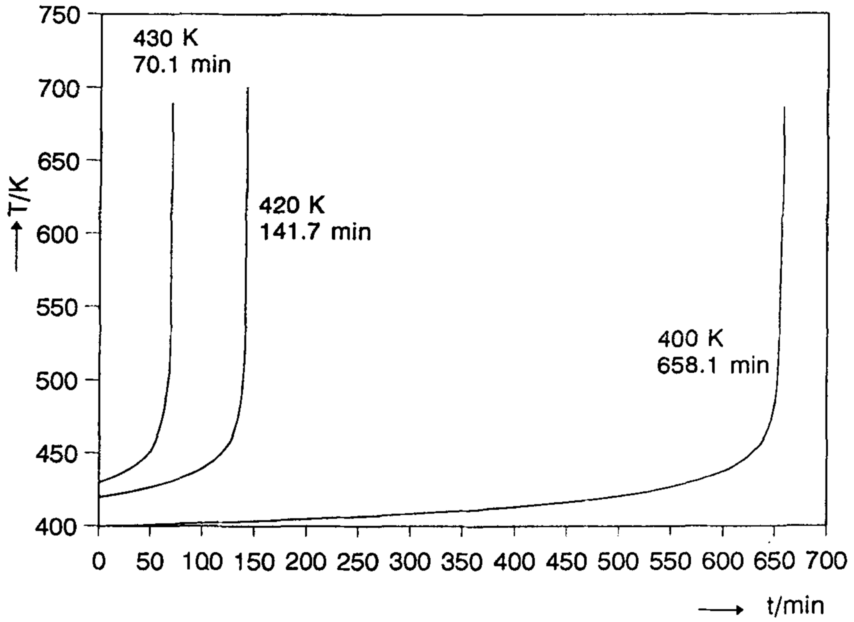

Fig. 4 Consecutive reaction, $k_2 >> k_1$, $\Delta T_{f1} = 150$ K, $\Delta T_{f2} = 150$ K, $E_1 = 115$ kJ·mol^{-1}, $E_2 = 84$ kJ·mol^{-1}, ln(k_{o1}min·mol) = 25, ln(k_{o2} min) = 25

is possible. Figure 4 shows typical *T*-*t*-curves for these types of consecutive reactions. Predetermination of the starting values by simulation is also possible.

In the other extreme case of Eq. (12b) we obtain *T*-*t*-curves as shown in Fig. 5. The temperature increase in the first step of reaction, until the induction time τ_i is reached, is almost exclusively due to the first reaction. Therefore, from this section of the curve, a direct parameter fitting for E_1 and ln k_{o1} is possible, on the basis of Eq. (11a). The second part of the curve can be used to determine the kinetic parameters E_2 and ln k_{o2}.

$$T = T_i + x_1\Delta T_{f1} + x_2\Delta T_{f2} \tag{13}$$

The value of x_2 can be computered using Eq. (13), because x_1 is available from the first part of curve. After this, the DE system of Eq. (11) provides the basis for the parameter fitting of E_2 and ln k_{o2}. Since E_1 and ln k_{o1} are predetermined, only two constants need to be computed by the non-linear searching strategy. To test this procedure of direct data fitting, computer simulated *T*-*t*-data have been used. In most cases, this is successful if the estimated starting values deviate by no more than 10% from the accurate ones.

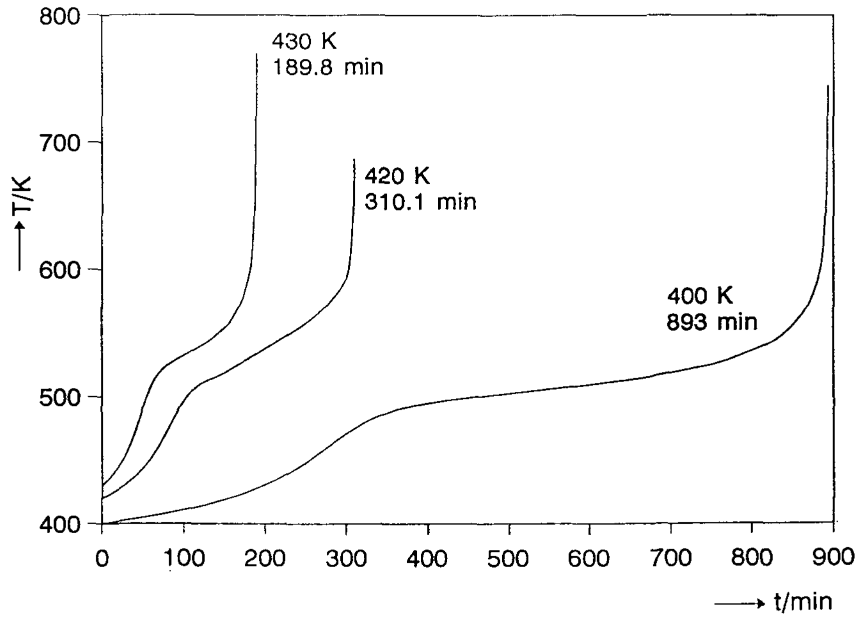

Fig. 5 Consecutive reaction, $k_1 >> k_2$, ΔT_{f1} = 100 K, ΔT_{f2} = 300 K, E_1 = 90 kJ·mol^{-1}, E_2 = 120 kJ·mol^{-1}, ln(k_{o1} min·mol) 25, ln(k_{o2} min) = 25

The determination of E_2 and ln k_{o2}, without using the second section of the curve, can give only a first approximation because of the influence of the first reaction and the lower precision of the measurements in this part.

Competitive consecutive reactions

This reaction type is described by Eq. (14a+b)

$$\mathrm{A + B} \xrightarrow{k_1} \mathrm{C} + \ldots.. \tag{14a}$$

$$\mathrm{A + C} \xrightarrow{k_2} \mathrm{E} + \ldots.. \tag{14b}$$

and has some aspects in common with the normal consecutive reactions (Eqs (9) and (10)). E.g., under the conditions k_1 equals to k_2, simulation of the T-t-curves is straight forward, but the determination of kinetic parameters by direct parameter fitting is not possible, because of the impossibility of separating k_1 and k_2.

The extreme case, $k_2 >> k_1$, leads, after an initial period, to x_1 equals to x_2, as was shown above. Therefore, the kinetic parameters are directly available if a satisfactory experimental *T-t*-curve is obtained. But, in contrast to the simpler consecutive reactions, the extents of reaction may only reach values of up to 0.5.

In the other extreme case, $k_2 << k_1$, essentially only the first of the two reactions occurs, i.e. the competitive consecutive reaction appears in the form of the simple reaction as discussed above.

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Zusammenfassung — In der chemischen Industrie gibt es oft Reaktionen, die mit großer negativer Enthalpieänderung ablaufen und manchmal technische Gefahren und Risiken, einschließlich Explosionen verursachen. Vorliegende Arbeit konzentriert sich auf die Untersuchung von adiabatischen Temperatur-Zeit-Kurven und erstellt nichtlineare Optimierungsprozeduren zur Ermittlung der kinetischen Parameter von einfachen Zersetzungsreaktionen, z.B. von o-Nitrobenzaldehyd, von zwei Typen von autokatalytischen Reaktionen, konsekutiven Reaktionen und kompetitiven konsekutiven Reaktionen. Der Vorteil dieses Rechenmodelles besteht darin, daß nur kinetische Differentialgleichungen benötigt werden.