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The calculation of adiabatic thermal explosion from isothermal DSC measurements

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Abstract

The calculation of thermal explosion conditions from results of micro-thermoanalytical measurements is often desirable and sometimes necessary because of the small amounts of material available. Diagrams of isothermal DSC experiments are particularly useful for providing measurements which can be evaluated by calculations of this kind.

These calculations are very simple for reactions which proceed according to well-defined *n*th-order kinetics, as with many reactions used in production processes. The well known theories of Semenov and Frank-Kamenetskii are suitable for this work. The calculation is not so trivial for exothermic decomposition reactions which usually follow an "autocatalytic" reaction mode. A method for such calculations is presented here.

For the determination of explosion conditions, isothermal DSC diagrams obtained at several temperatures are necessary. The autocatalytic reaction is characterized by two parameters of which at least one is temperature dependent. The differential equation for the adiabatic self-heating is solved numerically for the exothermic decomposition of several substances. The adiabatic induction times calculated are compared with the results of direct adiabatic measurements.

The satisfactory agreement of measured and calculated data show that calculation from isothermal results is a possible method. A small exothermic effect which appears in the first part of the isothermal DSC curve has to be taken into consideration, e.g. as a parallel first-order reaction, in order to get useful results.

1. INTRODUCTION

Exothermic decompositions under isothermal and adiabatic conditions are closely related to one another. If the isothermal decomposition behaviour is known over the entire temperature and conversion range of interest, then the adiabatic self-heating of the substance can be calculated. The reverse is also possible, but usually the isothermal measurements are easier and do not require the large sample quantities which are necessary for adiabatic tests.

The adiabatic self-heating which may result in a thermal explosion is important for the assessment of the safe handling of a product. The calculation of this adiabatic process from isothermal results, e.g. from isothermal DSC measurements, is a method which is frequently used. This calculation is complex because of the autocatalytic nature of many decomposition reactions.

A pure autocatalytic or branched-chain reaction implies a reaction rate which increases exponentially in the first part of the reaction. Consequently, the reaction rate may be very small at first. A competitive, non-autocatalytic reaction can have a large influence on the adiabatic self-heating although this effect may be very small. The discussion of these complications is the purpose of this paper.

2. FORMAL REACTION KINETICS OF EXOTHERMIC DECOMPOSITION

The kinetics of decomposition reactions which have been investigated up to now can be classified into two types.

1. Reactions which have their maximum rate at the beginning; the decrease in the isothermal reaction rate can be described by a rate equation of *n*th order, where *n* is often approximately 1.
2. Reactions which have at first a rather low isothermal rate; the rate increases and passes through a maximum.

The first type is found, for example, in decomposition reactions of diazonium salts, particularly in aqueous solution [1,2]. The elimination of nitrogen is a reaction which does not always lead to polymerization products. So a classical reaction mechanism is possible. Some substances of this type which have been proved to decompose by an approximately first-order reaction are shown in Table 1.

The second type is called "autocatalytic reaction". The autocatalysis generates an exponential increase of the isothermal reaction rate in the first part of the reaction. Most decomposition reactions appear to belong to this type. As this class of reaction is found with all types of molecular structures — inorganic and organic compounds — a general reaction mechanism seems to dominate. Brogli et al. [4] have found that many aromatic nitro compounds decompose according to this reaction type. In addition reaction masses containing nitro compounds showed this decomposition behaviour.

TABLE 1

Substances that show approximately first-order decomposition

Azoisobutyronitrile
Dimethyl 2,2′-azobisisobutyrate [3]
Phenylhydrazine
1,2-Diphenylhydrazine

TABLE 2

Substances that decompose autocatalytically

Nitrobenzene	Azoformamide
4-Nitrotoluence	Azobenzene
3-Nitrophenol	4-Chloro-1,2-diaminobenzene
4-Nitrobenzoic acid	4-Chloro-1,3-diaminobenzene
2-Nitrobenzaldehyde	4-Nitrosophenol
Sodium 3-nitrobenzene sulphonate	Ammonium dichromate
Benzaldoxime	Sodium azide

Substances for which the decomposition according to type 2 has been proved [5, 6] are shown in Table 2.

An important effect of autocatalysis in decomposition reactions is the reduction in the thermal stability of substances by isothermal storage at temperatures near the temperature region of decomposition. This effect has been described by Hentze and Krien [7].

Ideas for the explanation of these so-called "autocatalytic" reactions come from two directions. It was first encountered in the thermal decomposition of inorganic compounds, e.g. silver oxalate. In 1925 Macdonald and Hinshelwood investigated this reaction under rather low pressure [8]. They found an autocatalytic acceleration of the reaction and the formation of silver and carbon dioxide at low pressure, and concluded that the gaseous reaction product CO_2 could not be the autocatalyst. The reaction rate was not influenced by the particle size of the oxalate. Their conclusion was that the formation and growth of silver nuclei were essential for the rate of reaction.

The second field in which autocatalytic reactions are often observed is polymerization kinetics. As an example we refer to the polymerization of methyl methacrylate [9–11] which always shows a maximum reaction rate during the isothermal reaction. The reaction mechanism can be simply understood as the start and propagation of the polymerization reaction.

Thus a probable explanation for the very common autocatalytic decomposition is that it is connected with a polymerization process or the formation of a solid material.

3. DETERMINATION OF KINETIC DATA FROM ISOTHERMAL MEASUREMENTS

From isothermal measurements (e.g. by isothermal DSC), the formal kinetics of the heat production connected with a decomposition reaction can be determined. The results of these investigations contain all the information necessary for calculating the adiabatic self-heating of a substance. It is important to record isothermal diagrams of the rate of heat production at several temperatures in order to obtain complete information about the decomposition process. The temperature dependence of the reaction rate must be known for the calculation of an adiabatic temperature-time curve of a decomposition.

3.1. n*th Order reaction*

For the first-order decomposition the kinetic equation is

$$\mathrm{d}u/\mathrm{d}t = k(1-u) \qquad (1)$$

$$k = A\exp(-E/RT) \approx A\exp(-E/RT_0)\exp(E\theta/RT_0^2) \qquad (2)$$

where θ is the relative temperature and u the fractional degree of conversion. The most important property of an nth-order reaction is the fact that the reaction rate has its maximum value at the beginning. The order is not important because in the simple adiabatic calculation the decrease in reaction rate during the reaction is not taken into account. The value of k has to be determined at different temperatures in order to obtain the temperature dependence, eqn. (2).

3.2. *Autocatalytic reaction*

As already discussed, an autocatalytic reaction is the usually observed reaction type for exothermic decomposition reactions. Figures 1 and 2 show examples of isothermal DSC diagrams of compounds which decompose according to this reaction type.

The main difference between these reactions and those of nth order, is the rather low reaction rate at the beginning and the acceleration of the reaction. The reaction rate passes through a maximum and then decreases. The autocatalytic behaviour of the reaction is shown by the exponential increase in the first part of the reaction. It is not possible to find an approximately constant rate at the beginning of the reaction.

Although many decomposition reactions proceed according to the autocatalytic type, there are various deviations from the simplest model. The most obvious are

(i) the autocatalytic reaction is accompanied by a reaction of constant or slowly decreasing reaction rate;

(ii) the curve of reaction rate versus time has two maxima;

(iii) the fall-off of the reaction rate after the maximum is not symmetrical with the original rise of the curve.

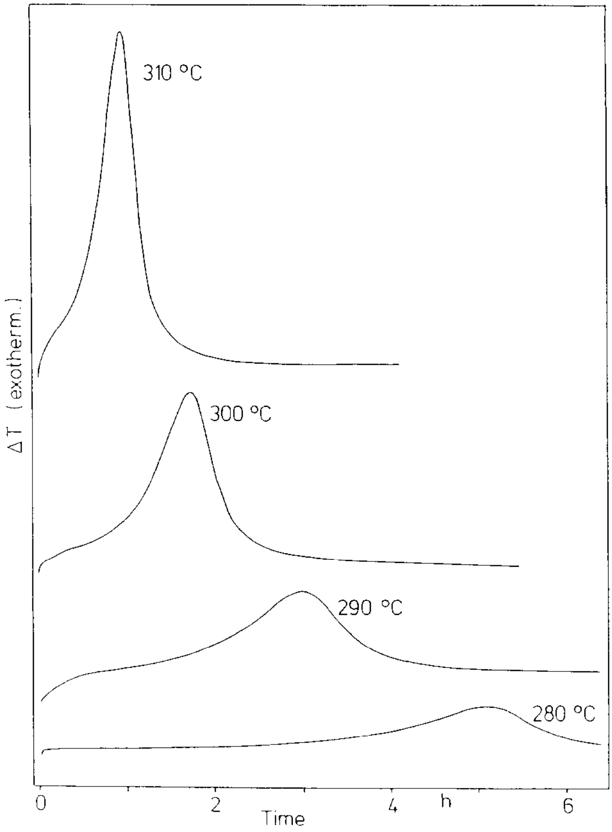

Fig. 1. Isothermal DSC diagrams of 4-nitrotoluene.

The first of these types seems to occur often and may be the source of serious errors in the calculation. The simple autocatalytic model involves an exponential increase of the reaction rate at the beginning of the reaction. If the degree of autocatalysis is large (i.e. β in the following calculation is very small), a small additive term will overcome the autocatalytic reaction at the beginning. If this is not noticed, the results of the calculation will be totally wrong. Two examples of this type will be discussed at the end of this paper.

The case of two or more maxima in the heat production curve can be solved by a somewhat more complicated mathematical model. Type (iii), the asymmetric form of the isothermal curve, implies no difficulties because the fall-off of the curve after the maximum has no importance for the adiabatic self-heating.

The differential equation for the simplest autocatalytic model is

$$\frac{\mathrm{d}u}{\mathrm{d}t} = k(1-u)(\beta+u) \qquad (3)$$

where u is the dimensionless fractional degree of conversion, k a first-order

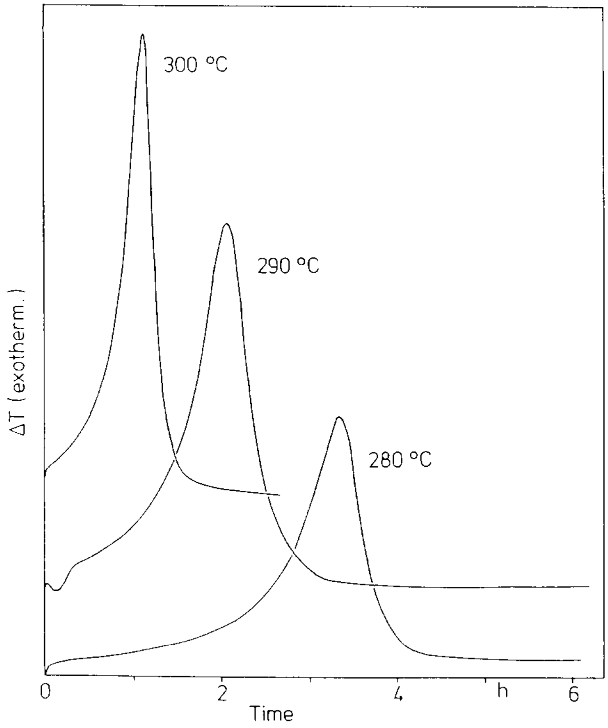

Fig. 2. Isothermal DSC diagrams of 3-nitrophenol.

reaction rate constant, and β the parameter of autocatalysis. A high degree of autocatalysis implies a small value of β.

For evaluating the DSC diagrams of autocatalytic decomposition, the constant β and k have first to be determined. The equation for the reaction rate r of the autocatalytic reaction under isothermal conditions is deduced from eqn. (3)

$$r \approx e^{kt}/(1+\beta\, e^{kt})^2 \qquad (4)$$

The isothermal DSC curve only fits this equation if the first increase of the reaction rate is an exponential function of time. To determine k and β from the DSC diagram, two equations are necessary. The time to maximum reaction rate $t_{\max}$ is very easily obtained from the DSC curve. From eqn. (4), a simple relationship between $t_{\max}$, k, and β can be derived

$$\beta \exp(kt_{\max}) = 1 \qquad (5)$$

A further equation can be derived which involves the time $t_{1/2}$ when the reaction rate is half the maximum rate. The difference between $t_{\max}$ and $t_{1/2}$ will be called $\Delta t_{1/2}$. From eqn. (4), the maximum reaction rate and the time of half maximum rate can be calculated. The following equation can be deduced

$$\exp(k\Delta t_{1/2}) = \sqrt{8} + 3 \qquad (6)$$

Equation (6), however, only gives a useful result if the reaction rate follows eqn. (4) very exactly. If eqn. (4) is only correct in the first part of the curve, a more useful method is to determine the exponential coefficient directly from the curve, which can be done by various numerical methods. This coefficient is k, and β can be calculated from eqn. (5). A disadvantage of this method is that for the reaction rate at the maximum of the isothermal curve, a wrong value is often calculated.

The test substances we used were 2-nitrobenzaldehyde, 4-nitrobenzoic acid, 4-nitrotoluene, and 3-nitrophenol. The kinetic constants of these substances, evaluated from isothoermal diagrams at different temperatures, are given in Table 3. The pre-exponential factor A and the activation energy E refer to the rate constant k.

The kinetic quantity β which characterizes the autocatalytic behaviour, cannot be determined very precisely; β often appears to increase with rising temperature, but this increase cannot be quantified very well. Isothermal DSC tests performed at the same temperature produced reproducible values of t_{max}, but not of β. The mathematical form of the kinetic equation, eqn. (4), is the reason for this behaviour: a variation of 10% in the ratio of $\Delta t_{1/2}$ to t_{max} generates a variation of 10% in k, but about a factor 10 in β.

Therefore, we chose the following method of evaluation. First k was determined from eqn. (6). Then β was calculated from eqn. (5). The geometric mean was calculated from the β values found in the temperature region which was important for the adiabatic calculation. From this mean value, the k values were calculated using eqn. (5). These mean values of k were used for the calculation of the Arrhenius parameters, in Table 3.

The adiabatic temperature increase ΔT_{ad} is also listed in Table 3; ΔT_{ad} was determined from decomposition energies which were obtained from temperature-programmed DSC diagrams. An estimated specific heat of

TABLE 3

Kinetic constants of autocatalytic decomposition evaluated from isothermal DSC diagrams

Substance	$^{10}\log A/\text{min}^{-1}$	$E/\text{kJ mol}^{-1}$	β	1st order fraction	$\Delta T_{ad}/\text{K}$
2-Nitrobenzaldehyde	11.30	110	0.04	–	300
4-Nitrobenzoic acid	10.67	128	5×10^{-9}	–	500
3-Nitrophenol	12.813	150	5×10^{-4}	0.014	800
4-Nitrotoluene	12.552	150	5×10^{-4}	0.017	500

$2\,\mathrm{J\,g^{-1}\,K^{-1}}$ was used. 2-Nitrobenzaldehye has a rather small ΔT_{ad} because the decomposition consists of two steps and only the first was considered.

For some substances (here, 3-nitrophenol and 4-nitrotoluene), the isothermal DSC diagrams show a heat production rate at the beginning which cannot be accounted for by the simple autocatalytic model. For these substances, the author has tried to use an additional first-order term in the reaction rate equation. Equation (3) was expanded to

$$\mathrm{d}u/\mathrm{d}t = k(1-u)(\beta + u) + kr_1(1-u) \tag{7}$$

where r_1 is the first-order fraction of the reaction and is, in our examples, less than 0.02. This relatively small fraction has a rather large influence on self-heating and adiabatic induction time, as the following calculations show.

4. CALCULATION OF THE ADIABATIC SELF-HEATING FROM THE KINETIC DATA

4.1. n*th Order reaction*

The order of the reaction is not important because the increasing conversion is not taken into account in further deductions. If the heat of the exothermic reaction is high, the reaction rate does not change very much during the time which is necessary for the initiation of the thermal explosion. The equations for the adiabatic thermal explosion as derived in Frank-Kamenetzkii [12] are

$$\tau_{\mathrm{ad}} = (k_0 B)^{-1} \tag{8}$$

$$B = E\Delta T_{\mathrm{ad}}/RT_0^2 \tag{9}$$

where k_0 is the rate constant at the starting temperature of the decomposition. This result means that the adiabatic induction time is the isothermal reaction time at the starting temperature k_0^{-1} divided by the reaction number B.

4.2. *Autocatalytic reaction*

In the adiabatic case the temperature rises according to

$$T = T_0 + u\Delta T_{\mathrm{ad}} \tag{10}$$

The temperature influences the kinetic equation through the temperature dependence of k

$$k = A\exp(-E/RT)$$

A combination of the three equations (2), (7) and (10) can only be resolved by numerical methods. An analytical solution is possible if β independent of temperature, if the term u is neglected in $(1-u)$, and if the Frank-Kamenetzkii abbreviation is used for $\exp(-E/RT)$. The solution is

$$\tau_{ad} = k_0^{-1} \exp(\beta B) E_1(\beta B) \qquad (11)$$

where E_1 is the exponential integral, a function which can be looked up in mathematical tables. This approximation is often unsatisfactory, and a numerical evaluation is necessary.

To examine the accuracy of this type of calculation, we used the substances mentioned above. The adiabatic measurements were performed using Dewar methods. The results are graphical representations of the adiabatic induction time plotted in a logarithmic scale versus the reciprocal absolute temperature.

Using the quantities β and k (that is, A and E) and r_1 from Table 3, we have calculated the adiabatic self-heating starting at several temperatures. The temperature-time curves represented in Figs. 3 and 4 were calculated for the examples 4-nitrotoluene and 3-nitrophenol, and were plotted by the computer. From Fig. 3, the adiabatic induction times of 4-nitrotoluene have been taken and were plotted as shown in Fig. 5. The adiabatic induction time is defined as the time which is needed for the self-heating from the start temperature (storage temperature) to the time of maximum rate. Figure 5 is the graphical representation of induction times in logarithmic scale versus $1/T$. In this figure we have represented four types of induction time as stright lines: the adiabatic induction time (experimental) from ref. 6; the isothermal induction time t_{max} from our measurements; adiabatic

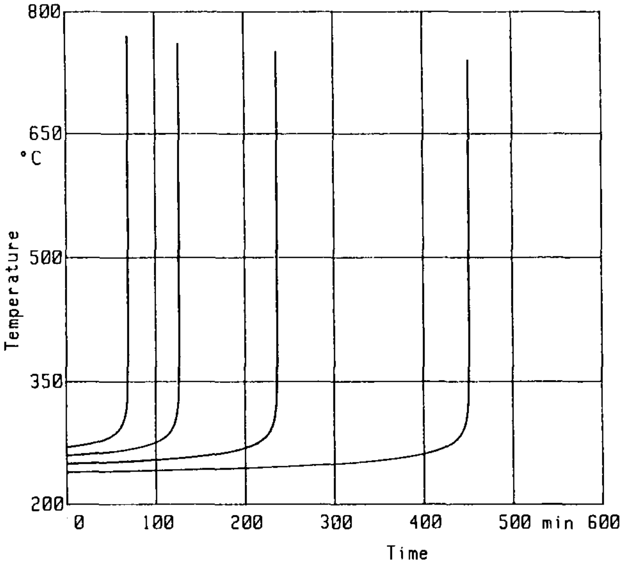

Fig. 3. Temperature-time curves of the adiabatic decomposition of 4-nitrotoluene calculated using data from Table 3. $T_0 = 240$, 250, 260, and 270°C.

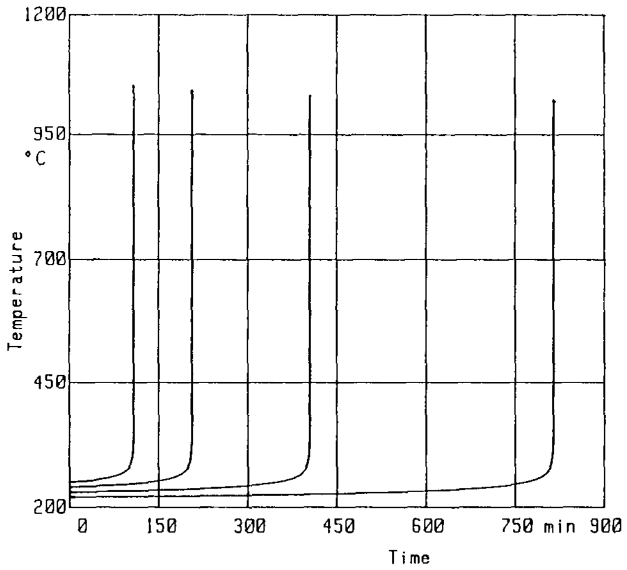

Fig. 4. Temperature-time curves of the adiabatic decomposition of 3-nitrophenol calculated using data from Table 3. $T_0 = 220$, 230, 240, and 250°C.

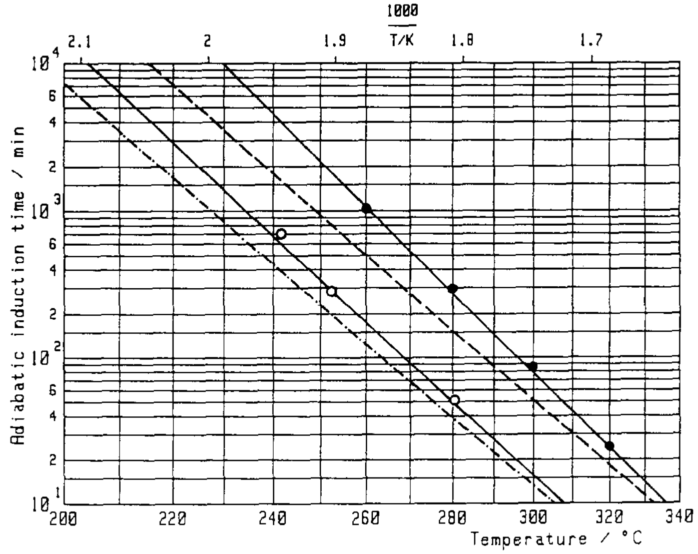

Fig. 5. Adiabatic induction times of the decomposition of 4-nitrotoluene: ●, isothermal induction time (t_{max}); ○, measured adiabatic induction times [6]; ---, adiabatic induction times, calculated with $r_1 = 0$; and -·-·-, adiabatic induction times, calculated with $r_1 = 0.017$ (from Fig. 3).

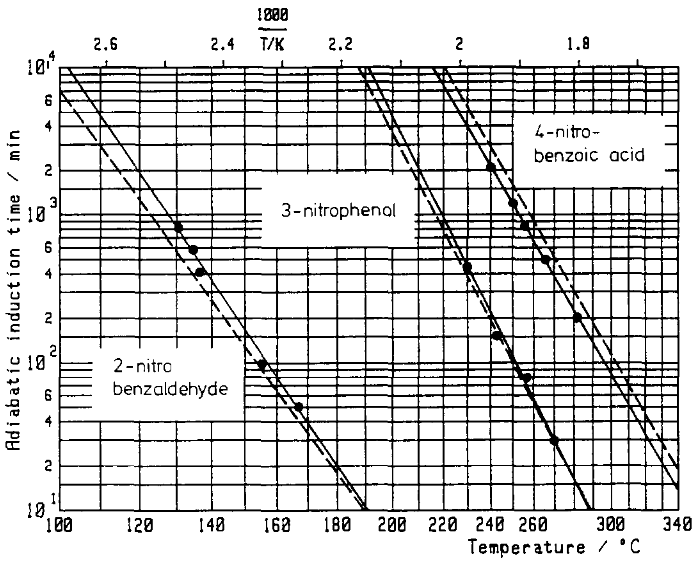

Fig. 6. Adiabatic induction times of three nitro compounds: ●, measured [6]; and ---, calculated (using data from Table 3).

induction times calculated without the first-order term; and adiabatic induction times calculated with the additional r_1 term.

Figure 5 shows a satisfactory agreement between the measured adiabatic induction times and those calculated using an additional first-order term. For 2-nitrobenzaldehyde and 4-nitrobenzoic acid, we did not see an additional kinetic term in the isothermal DSC diagrams.

For 2-nitrobenzaldehyde, 3-nitrophenol, and 4-nitrobenzoic acid, the results are represented in Fig. 6 which shows the measured [6] and calculated (from the data of Table 3) adiabatic induction times. The agreement is satisfactory.

5. CONCLUSIONS

The method of calculating adiabatic self-heating from isothermal measurements, particularly for exothermic decomposition reactions, has been discussed on the basis of experimental results. The kinetic evaluation of the isothermal measurements usually suggests an autocatalytic reaction type. A strongly autocatalytic reaction is very slow at first, before the acceleration due to the autocatalytic effect begins. A weak parallel non-autocatalytic reaction can be much stronger than the autocatalytic reaction in the beginning, and thus accelerates the adiabatic self-heating in the first stage.

The decomposition reactions of four aromatic nitro compounds were used for testing the accuracy of the calculation. The isothermal as well as the adiabatic reactions were measured in our laboratory. Two of these substances showed a small non-autocatalytic effect in isothermal DTA. The calculation of the adiabatic self-heating generated erroneous results if the weak parallel reaction was not taken into account. When the weak parallel reaction, which was assumed to be of first order, was used as an additional term in the self-heating equation, satisfactory results were obtained.

Our conclusion is that in the evaluation of isothermal measurements it is necessary to look out for weak parallel exothermic reactions and to consider them in the calculation.

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