Chimia 48 (1994) 542–550
© Neue Schweizerische Chemische Gesellschaft
ISSN 0009–4293

The Thermal Risk of Autocatalytic Decompositions: A Kinetic Study

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Abstract. A method is presented for the estimation of the 'time to maximum rate under adiabatic conditions' of autocatalytic decompositions and for their safety assessment. This method is based on the kinetics: a first-order reaction in competition with a *Prout-Tompkins* step was choosen. Isothermal or temperature-programmed Differential Scanning Calorimeter curves were used to obtain the kinetic parameters. The method requires the heat release rates at the start of the reaction and at its maximum. It is in agreement with previously published ones, but is more easy to apply and allows, therefore, to performe a quick assessment of the safety of a process. Results found for the adiabatic case were confirmed by Accelerating Rate Calorimeter experiments.

1. Introduction

Traditionally, risk is defined as the product of the severity of a potential incident by its probability of occurrence. Considering chemical decompositions, their reaction energy can be taken as a measure of the severity whereas their probability is linked to the time to Explosion.

Very often an originally desired reaction is the cause of an incident. A desired reaction can constitute a thermal risk, if its control is lost and a runaway reaction is, therefore, triggered. Hence, it is necessary to understand how a reaction can change from its normal course to a runaway reaction, and then to plan countermeasures. This can best be done within the frame of a risk analysis which is based on a systematic approach, such as a defined runaway scenario [1]. Since in a large reactor (>1 m^3) without an efficient and active cooling system, heat dissipation is negligible compared to the heat-release rate of the reaction going on in the batch, the situation can be considered adiabatic.

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Such a scenario will, therefore, describe the temperature time behavior in the adiabatic case. The resulting temperature increase is proportional to the severity of the potential incident: the higher the temperature and the pressure, the more heavy are the consequences. The kinetics of the reaction, on the other hand, determines the runaway time: countermeasures cannot be taken and the risk, therefore, not be controlled, if the reaction is too fast or the time to explosion too short. An estimate of this time can be obtained by using the concept of the *T*ime to *M*aximum *R*ate under *ad*iabatic conditions (TMR_{ad}).

$$TMR_{ad} = (c_p\, R\, T_0^2)/(q_0\, E_a)$$

This approximation [2] is valid for reactions of zero order. The error is low for other reaction orders, if the reaction in question is very exothermic. In this case, the temperature increase is high even at low conversion, and the reaction rate is almost independent of the conversion.

A decomposition reaction has, however, often an autocatalytic mechanism. Such a reaction can be formally represented by a mechanism involving two parallel steps: the first one is a first-order reaction, whereas the second one is of a second order, *Prout-Tompkins*, reaction type:

$$A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} 2B$$

Sometimes the reaction seems to be preceded by an induction time during which no exothermic reaction can be observed. In this case, one could calculate the activation energy and the TMR_{ad} using the maximum rate of heat release and neglecting the induction time. This leads to induction times which are too short and therefore, to enormous safety margins in time. The apparent risk could eventually prevent an interesting process from being commercially exploited.

The aim of this paper is to develop an estimation method for the time to explo-

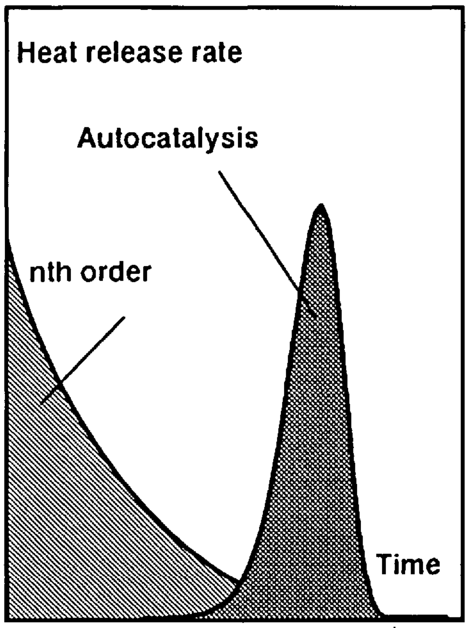

Fig. 1. *Autocatalysis and reaction of* nth *order under isothermal conditions*

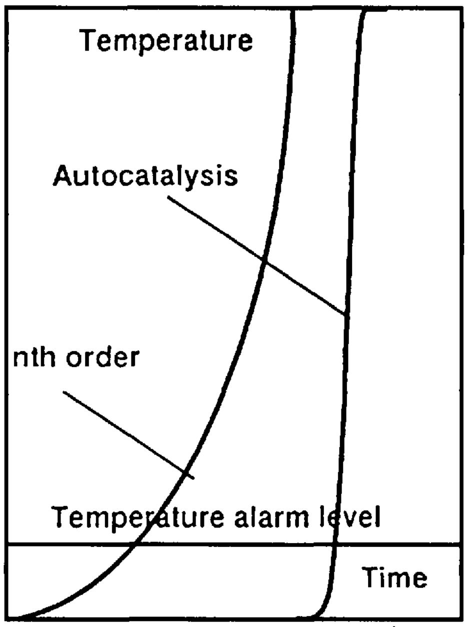

Fig. 2. *Autocatalysis and reaction of* nth *order under adiabatic conditions*

CHIMIA 48 (1994) Nr. 12 (Dezember)

sion under adiabatic conditions in the case of autocatalytic decomposition reactions.

The method should be reliable and easy to use. It should require only instruments commonly used in thermal safety laboratories like Differential Scanning Calorimeters (*DSC*) and possibly an Accelerating Rate Calorimeters (*ARC*). The method is demonstrated using 2,4-dinitrophenol (2,4-DNP) as a test substance.

2. Definition of an Autocatalytic Reaction and of the Macro-kinetic Model

Reactions often follow an n^{th} order kinetic law. Under isothermal conditions, *i.e.*, conditions, where the temperature remains constant, the heat release rate decreases uniformly in time. In the case of an autocatalytic decomposition, the behaviour is quite different (*Fig. 1*).

An acceleration of the reaction rate with time is observed. The corresponding heat-release rate passes through a maximum and then decreases again. Hence, an isothermal *DSC* experiment will immediately show to which type a reaction belongs. In the case of an adiabatic runaway, these two types of reaction will lead to totally different temperature *vs.* time curves: with n^{th} order reactions, the temperature increase starts immediately after the cooling failure, while with autocatalytic reactions the temperature remains stable during the induction period and then suddenly increases very sharply (*Fig. 2*).

For the design of emergency measures, it is very important to know to which of the two types a decomposition reaction belongs. For example, temperature alarms will only be useful with decomposition reactions following an n^{th} order kinetic law, as only in these cases the warning time will be sufficiently long.

Several existing models describe the autocatalytic behavior of a reaction. The best known and the oldest one (1945) is the *Prout-Tompkins* model [3–8]:

$$A + B \xrightarrow{k} 2B$$

This model was developed to describe the thermal decomposition of permanganates. The reaction rate $r = k\,[A][B]$ shows a quadratic dependence.

A corresponding cubic dependence [9–11] can be described by:

$A + 2B \xrightarrow{k} 3B$ and the reaction rate becomes $r = k\,[A][B]^2$.

To describe the decomposition of many apparently pure products, these models are not suitable as the impurity, *i.e.*, the catalyst, must be already present. Therefore, an initiation reaction which produces the catalyst is postulated, resulting in the following model [12]:

$$\nu_1 A \xrightarrow{k_1} \nu_1 B$$

$$\nu_2 A + \nu_3 B \xrightarrow{k_2} (\nu_3 + 1)B$$

$$r = k_1\,[A]^a - k_2\,[A]^b\,[B]^c$$

As simplification we set $\nu_1 = \nu_2 = \nu_3 = 1$ and $a = b = c = 1$:

$$A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} 2B$$

$$r = k_1\,[A] - k_2\,[A][B]$$

This simplification will in general underestimate the adiabatic runaway time of reactions of higher orders. This error is on the safe side and can be tolerated.

This model has already been discussed by *Schmid* and *Sapunov* [13], *Boldyreva* [14], *Chen* and *Reagan* [15], *Benito-Perez et al.* [16][17], *Ordax* and *Arrizabalaga* [18]. *Grewer* and *Klais* [19] gave special attention to the thermal process safety.

It should be noted that there is a difference between self-accelerating and autocatalytic reactions. Self-accelerating reactions are not always autocatalytic. The rate of autocatalytic reactions increases with the concentration of a catalyst [B] formed by the reaction itself.

A delay in product formation or heat release rate and, therefore, a self acceleration of the reaction can, however, be produced by another than an autocatalytic mechanism. Let us consider a system with two consecutive reactions

$$C \xrightarrow{k_1} D \xrightarrow{k_2} E$$

The rate of reaction $d[D]/dt$ will reach a maximum when

$$\frac{d[D]}{dt} = k_l[C] - k_2[D] = 0$$

at the time [20–22] $t'_{max} = \dfrac{k_1 \ln\,[k_1/k_2]}{1-(k_2/k_1)}$

if, moreover, only the second step is exothermic or very fast, a delay in the heat-release rate will be observed (*Fig. 3*).

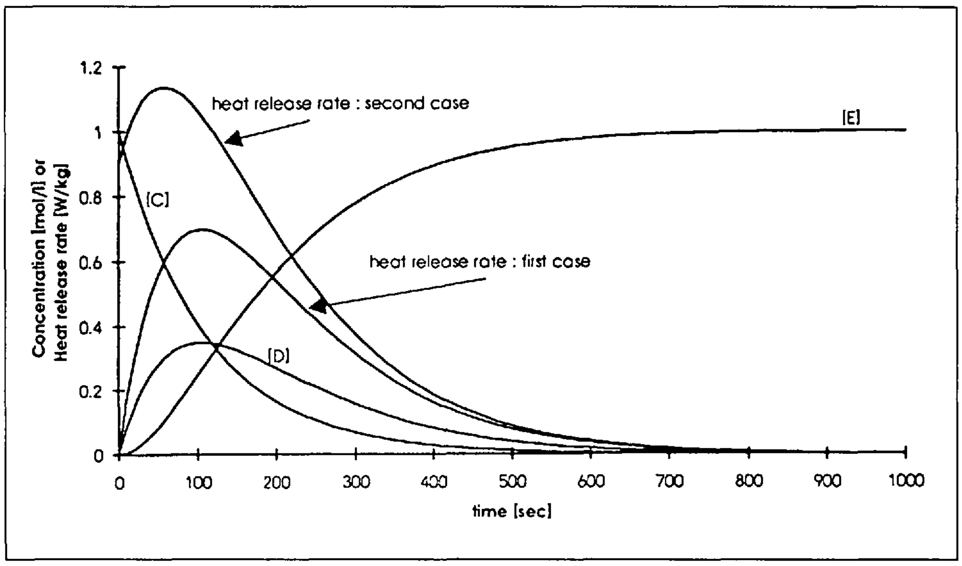

Fig. 3. *Consecutive reaction: concentration and heat release rate as a function of the time* ($[A]_0 = 1$ mol · l^{-1}, $k_1 = 0.01$ mol · l^{-1} · s^{-1}, $k_2 = 0.1$ mol l^{-1} · s^{-1}, $H_2 = -200$ J · mol^{-1}, $H_1 = 0$ (first case) and -100 J · mol^{-1} (second case))

3. Experiments

2,4-Dinitrophenol (2,4-DNP, *Fluka 42160*) was used without further purification and its initial concentration in all experiments is $[A]_0 = 5.43$ mol · kg^{-1}. *DSC* curves were obtained using sealed stainless crucibles purchased from *Mettler-Toledo*. The study was carried out under different atmospheres: Ar – N_2 – O_2 – ambient air and compressed air. No reproducible results were obtained in ambient air under isothermal conditions. The induction time of the decomposition obviously depends on the moisture content of the air (*Fig. 4*). Therefore, all *DSC* and *ARC* experiments with this substance were carried out under an Ar atmosphere.

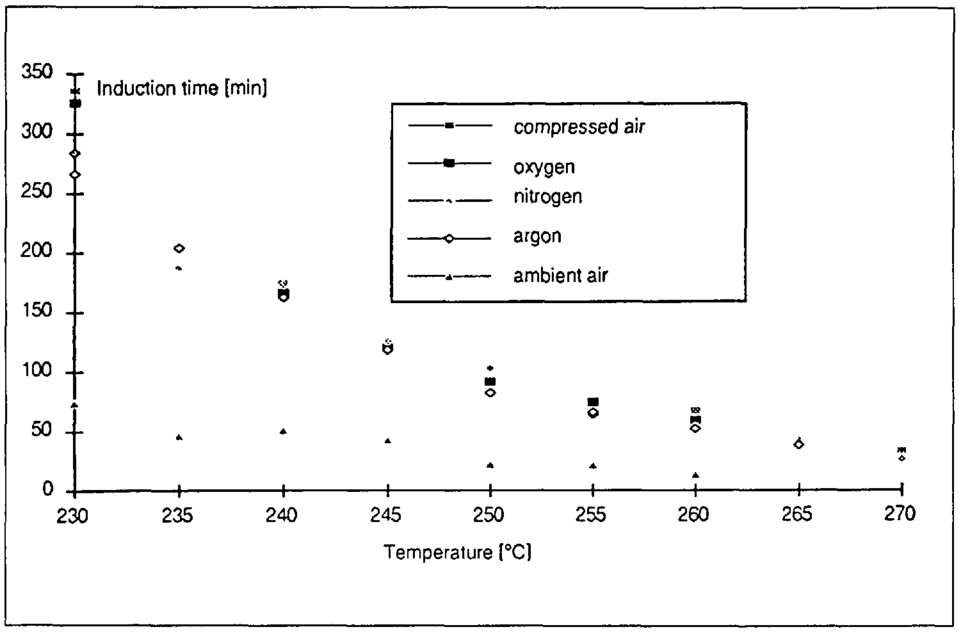

Fig. 4. *Thermal stability of 2,4-DNP under different atmospheres*

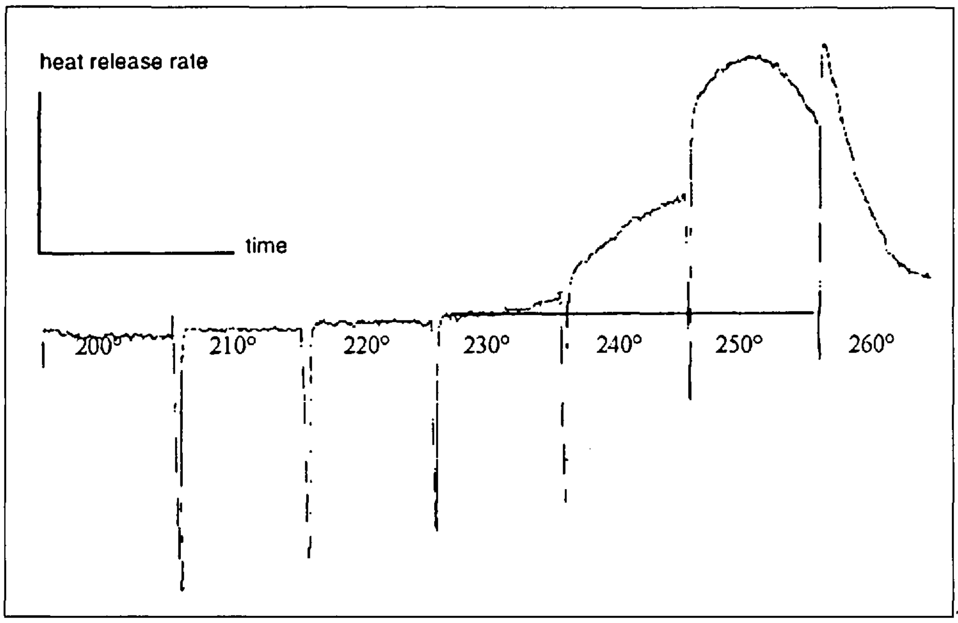

Fig. 5. *The 'heat, wait, and search' procedure of the ARC simulated by an isothermal DSC measurement*

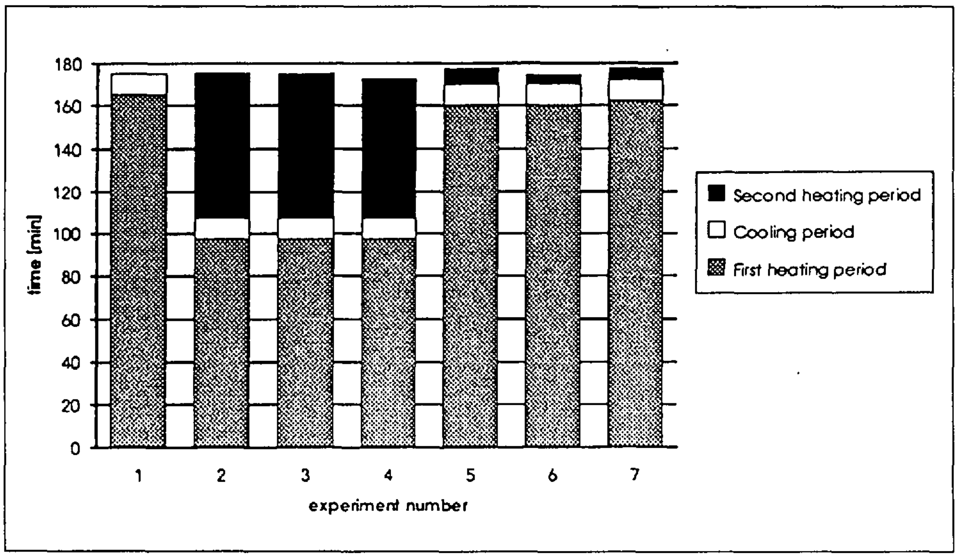

Fig. 6. *Thermal history of 2,4-DNP: the catalysator is not affected by the cooling period*

One of the most common anal. techniques utilized in assessing thermal reaction hazards is *DSC* [23][24]. *DSC* experiments were carried out using *Mettler DSC25* and *DSC820* ovens with the *TA4000* and *TA8000* evaluation systems, resp.

In both isothermal DSC and ARC measurements, the reaction is initiated thermally: the temp. is raised to the desired level and then allowed to reach an equilibrium. During this period, no signal can be measured, although the heat release rate of the reaction and, therefore, the conversion may be noticeable.

In the case of an isothermal *DSC*, a blank may be run and the true initial heat-release rate obtained. In isothermal *DSC* measurements, the baseline is usually considered to be a horizontal straight line up to the end of the measurement.

In order to know at which temp. T_i the *ARC* experiment should be started using the 'isothermal age' modus, the 'heat, wait and search' procedure of the *ARC* was simulated by an isothermal *DSC* measurement using a stepwise increase of temp. To take into account the different sensitivities of *DSC* and *ARC*, the actual T_i for the *ARC* was chosen 30° below the first exotherm observed in the preliminary *DSC* experiment (*Fig. 5*).

For the kinetic evaluation of temp. programmed *DSC*-curves the *Netzsch* [25] program (thermokinetic analysis, version multiple scan) was used. Numerical solutions of differential equations were obtained with the *Isim* [26] simulator.

4. Thermal History of Samples

Fig. 6 shows the overall induction time, under isothermal conditions, for samples with different temperature-time treatment. The sample is kept for a certain time at 240° (first heating period), cooled down and heated again to 240° (second heating period). An acceleration of the decomposition is observed, compared to the freshly prepared sample (first experiment). However, the induction time (sum of the first and the second one) is nearly the same regardless of the thermal treatment.

The formed catalyst is stable even at low temperatures and accelerates the decomposition. This has important consequences for industrial processes with pronounced residence times, *e.g.* continuous rectification or batch distillations. It is indeed usual in production that the distillation residue is left in the kettle and mixed with the following batch. In such a case the decomposition will be accelerated.

5. Evaluation of DSC Measurements

The heat-release rate of a chemical reaction is a function of both temperature and conversion rate. The complete thermokinetic description of a decomposition reaction involves, therefore, the knowledge of both factors separately. By using a series of isothermal measurements, in which the temperature is kept constant, the conversion rate as a function of the time can be measured separately.

5.1. *The Isothermal Mode*

The decrease of species A can be described by *Bernoulli*'s differential equation:

$$-\frac{d[A]}{dt} = k_1\,[A] + k_2\,[A]\,([A]_0-[A]) \quad (1)$$

The solution of *Eqn. 1* is given by *Benito-Perez* [17]:

$$[A] = \frac{k_1 + k_2\,[A]_0}{k_2 + \frac{k_1}{[A]_0}\exp\,[(k_1 + k_2\,[A]_0)\,t]} \quad (2)$$

The instantaneous heat release rate, dq/dt, as measured by *DSC*, is proportional to d/dt where α is the conversion:

$$\alpha = \frac{[A]_0 - [A]}{[A]_0} \quad (3)$$

$$dq/dt = (-\Delta H_r)\,d\alpha/dt \quad (4)$$

Insertion of [A] as defined by *Eqn. 2* in *Eqns. 3* and *4* gives:

$$\frac{dq}{dt} = -\Delta H_r\,\frac{k_1\,(k_1 + k_2[A]_0)^2\exp[(k_1 + k_2[A]_0)\,t]}{(k_2\,[A]_0 + k_1\exp\,[(k_1 + k_2[A]_0)\,t])^2} \quad (5)$$

Simplification: For the most common case where $k_2[A]_0 >> k_1$, *Eqn. 5* becomes:

$$\frac{dq}{dt} = -\Delta H_r\,\frac{k_1\,(k_2[A]_0)^2\exp[(k_2[A]_0)t]}{(k_2\,[A]_0 + k_1\exp\,[k_2[A]_0\,t])^2} \quad (6)$$

and the conversion:

$$\alpha = \frac{k_1\exp[k_2[A]_0\,t]}{k_2\,[A]_0 + k_1\exp\,[\,k_2[A]_0\,t]} \quad (7)$$

Conversion at the maximum heat release rate: It can be shown that the maximum α_{max} of $\alpha = f(t)$ is found for $d^2\alpha/dt^2 = 0 = d^2q/dt^2$, which corresponds to the maximum heat release rate in *Eqn. 5*.

$$\alpha_{max} = \frac{k_2[A]_0 - k_1}{2\,k_2\,[A]_0} \quad (8)$$

Using *Eqn. 8* with $k_2[A]_0 >> k_1$, α_{max} is shown to be 0.5. (9)

Therefore, the maximum heat-release rate is obtained when half of the reactant [A] is used.

5.1.1. *Determination of Kinetic Parameters: First Method*

In isothermal mode, the kinetic parameters are both rate constants, k_1 and k_2, and the activation energies, E_{a1} and E_{a2}.

The rate of increase of the product B is given by:

$$\frac{d[B]}{dt} = k_2\,[A][B] + k_1\,[A] \quad (10)$$

If $[B] = \alpha\,[A]_0$, then:

$$[A] = [A]_0 - \alpha\,[A]_0 \quad (11)$$

Using *Eqn. 11, 10* becomes:

$$\frac{d\alpha}{dt} = k_2\,(1-\alpha)\,(\alpha + \frac{k_1}{k_2\,[A]_0}) \quad (12)$$

Eqn. 12 is similar *Grewer*'s expression [27] with $\alpha = u$, $k_2 = k$ and $\beta = k_1/k_2\,[A]_0$, u, k and β being notations used by this author.

In the case of existing traces of B in the starting system, that is to say, $[B]_0$,

$$\alpha\,[A]_0 = [B] - [B]_0 \quad (13)$$

Eqn. 12 then gives:

$$\frac{d\alpha}{dt} = k_2\,(1-\alpha)\,(\alpha + [B]_0/[A]_0) \quad (14)$$

where $[B]_0$ replaces k_1/k_2, *i.e.* there is a formal similarity between the chosen model and the *Prout-Tompkins* model with an initial concentration of catalyst.

The integration of *Eqns. 12* or *14* gives:

$$\alpha\,[A]_0 = \frac{[B]_0\exp(k_2([A]_0 + [B]_0)t) - 1}{1 + \frac{[B]_0}{[A]_0}\exp(k_2([A]_0 + [B]_0)t)} \quad (15)$$

By introducing the dimensionless parameter $\alpha_0 = [B]_0/[A]_0$. (16)
the solution of *Eqn. 14* for α gives:

$$\alpha = \frac{\alpha_0\,[\exp((1+\alpha_0)\,k_2[A]_0t) - 1]}{1 + \alpha_0\exp((1+\alpha_0)\,k_2[A]_0t)} \quad (17)$$

If $[B]_0 \approx 0$, $\alpha_0 \rightarrow 0$, therefore, *Eqn. 17* can be written as:

$$\frac{\alpha}{1-\alpha} = \alpha_0\exp\,(k_2[A]_0t) \quad (18)$$

This equation can be linearised by taking the ln of *Eqn. 18*:

$$\ln\frac{\alpha}{1-\alpha} = \ln\alpha_0 + k_2[A]_0t \quad (19)$$

Application: α is the conversion yield of the reaction referred to intermediate products, *i.e.*, products directly responsible for the autocatalysis. α is thus deduced from isothermal *DSC* measurements.

$$\alpha = \frac{(-\Delta H_r) - (-\Delta H_t)}{(-\Delta H_r)} \quad (20)$$

Thus, $f(\alpha) = \ln\,[\alpha/(1-\alpha)]$ may be plotted as function of time. The slope of the straight line (*Fig. 7*) is then $k_2[A]_0$; furthermore, for $\ln\,[\alpha/(1-\alpha)] = 0$, the following equation is obtained:
$\ln\alpha_0 = -k_2[A]_0t$,
thus $\alpha_0 = [B]_0/[A]_0 = k_1/k_2[A]_0$ and k_1 can be deduced.

α_0 can be considered as the degree of autocatalysis of the reaction. A small value of α_0 corresponds to a high degree of autocatalysis.

This method [28] was used by *Larionova et al.* [29], *Boldyreva* [14], and *Sakurai et al.* [30] in a different area of thermal analysis.

Results of this method are summarized in *Table 1*.

Values found using this method allow an estimate of activation energies and pre-exponential factors (*Table 2*) using a simple *Arrhenius* diagram.

CHIMIA 48 (1994) Nr. 12 (Dezember)

5.1.2. *Determination of Kinetic Parameters: Second Method*

This simple method is applicable only for a low degree of autocatalysis, *i.e.*, for cases with a measurable initial heat release rate.

Using *Eqn. 5* we obtain $k_1(-\Delta H_r)$ for $t = 0$, which corresponds to the initial heat release rate q_{ref1} as measured by *DSC*. Thus an estimate of k_1 may be obtained:

$$k_1 = q_{ref1}/(-\Delta H_r). \qquad (21)$$

Using *Eqn. 2* and its derivative with respect to time $d[A]/dt$, it can be written:

$$\frac{1}{[A]^2}\frac{d[A]}{dt}(-\Delta H_r) = -\frac{k_1}{[A]_0}(-\Delta H_r)\exp[(k_1 + k_2[A]_0)t] \qquad (22)$$

Also using *Eqn. 3*, the left hand side of *Eqn. 22* can be expressed as:

$$\frac{1}{[A]^2}\frac{d[A]}{dt}(-\Delta H_r) = -\frac{1}{[A]_0(1-\alpha)^2}(-\Delta H_r)\frac{d\alpha}{dt} \qquad (23)$$

Using *Eqns. 7* and *9*, the time t_{max} at which the maximum heat release rate is observed, is given by:

$$t_{max} = (1/(k_1 + k_2[A]_o))\ln[k_2[A]_0/k_1] \qquad (24)$$

Eqns. 22 and *23* can be set equal for $t = t_{max}$ and $\alpha = \alpha_{max} = 0.5$:

$$4(-\Delta H_r)\left(\frac{d\alpha}{dt}\right)_{t=t_{max}} = -k_2[A]_0(-\Delta H_r) \qquad (25)$$

The maximum heat release rate q_{ref2} in the left hand side of *Eqn. 25* can be expressed as:

$$q_{ref2} = (-\Delta H_r)\left(\frac{d\alpha}{dt}\right)_{t=t_{max}} \qquad (26)$$

The rate constant of the autocatalytic reaction may then be written using *Eqns. 25* and *26*:

$$k_2 = \frac{4\,q_{ref2}}{(-\Delta H_r)[A]_0} \qquad (27)$$

Comparison of both methods: The second method is compared to the first one in *Table 1*. Values of activation energies can be seen in *Table 2*.

Both methods give, within 1%, the same results. Small variations (~ 1%) in activation energy values have no influence on the result of the simulation: simulated curves can be superimposed. Using the above determined parameters and *Eqn. 6*, isothermal *DSC* curves can be numerically calculated (*Fig. 8*).

In general, the first method is always more precise, because all the points of the curves are used to estimate parameters. Only two points are used in the second one.

The second method is, therefore, more easy to apply, as only reference powers are required. This method may thus be used for a quick decision on the probability of occurrence. But it is unsuitable when there is no measurable initial heat release rate, that is to say, when q_{ref1} is lower than the detection limit of the *DSC* device *i.e.* for a high degree of autocatalysis.

5.2. *The Temperature-Programmed Mode*

This mode allows an estimate of the energy and of the temperature range within which the undesired reaction will occur.

Table 1. *Reference Powers* (each value is the mean of 6 experimental values) *and Estimating of Tate Constant, Based on Method 1 and 2*

Temp. [°]	q_{ref1} [W/kg]	q_{ref2} [W/kg]	First method $k_1 \cdot 1000$ [s^{-1}]	First method $k_2 \cdot 1000$ [$kg \cdot mol^{-1} \cdot s^{-1}$]	Second method $k_1 \cdot 1000$ [s^{-1}]	Second method $k_2 \cdot 1000$ [$kg \cdot mol^{-1} \cdot s^{-1}$]
230	8	169	0.0025	0.038	0.0026	0.039
240	10	371	0.0032	0.094	0.0031	0.085
250	13	814	0.0042	0.194	0.0042	0.192
260	36	987	0.0110	0.235	0.0115	0.228
270	76	1894	0.0236	0.437	0.0233	0.448

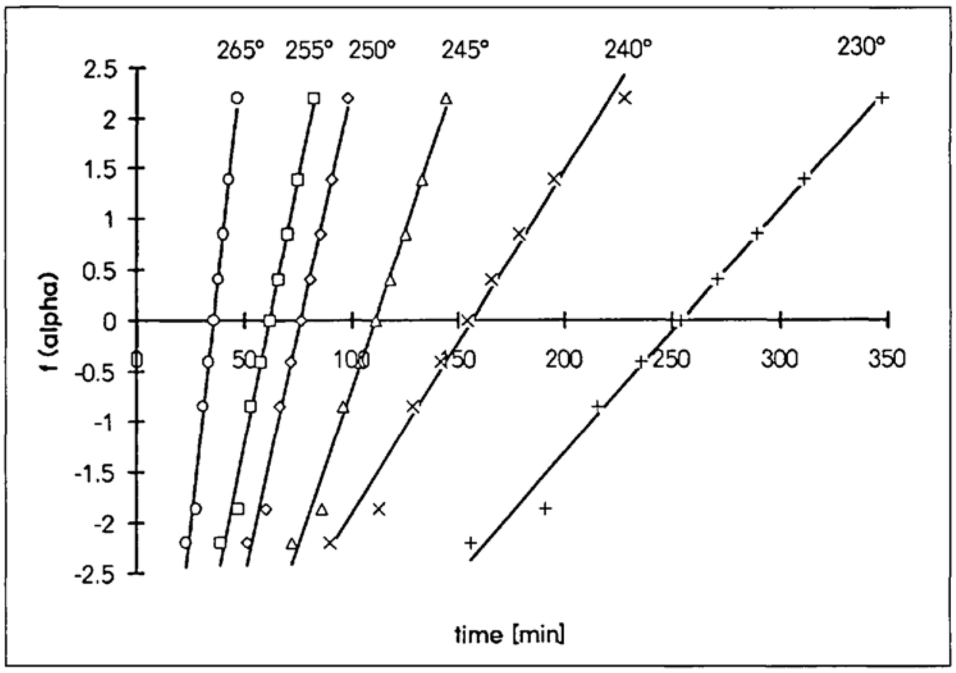

Fig. 7. *Illustration of the first method:* Eqn.19 *as a function of the time for different isothermal temperatures*

CHIMIA 48 (1994) Nr. 12 (Dezember)

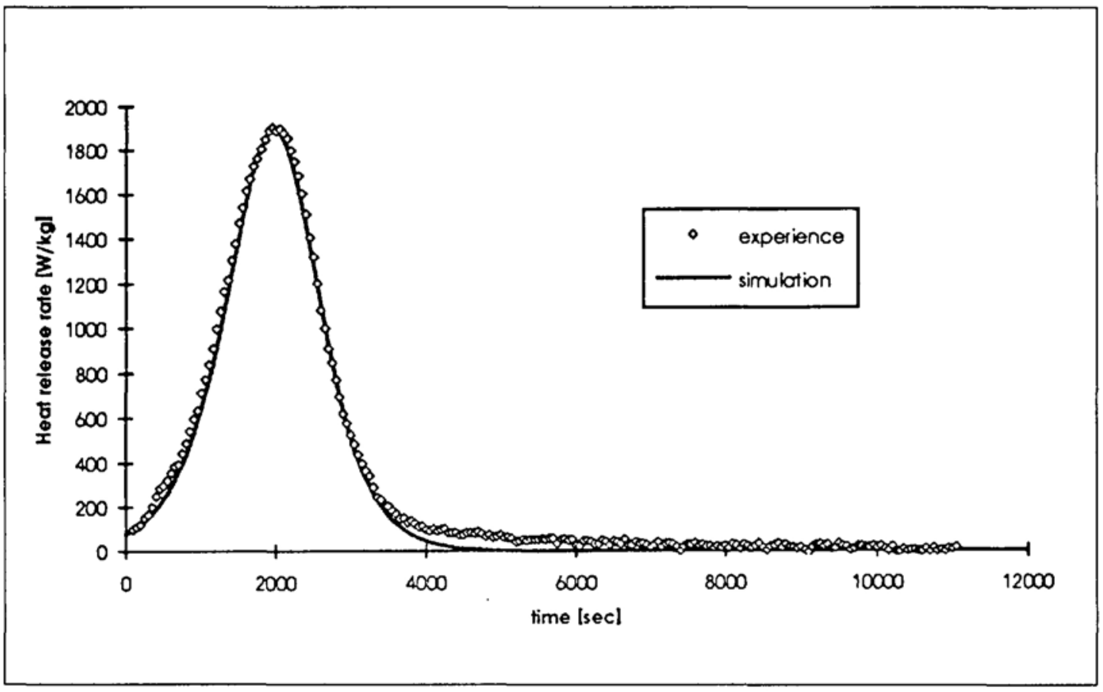

Fig. 8. *Experimental and simulated curves of an isothermal measurement of 2,4-DNP:* T_{iso} = *270°*

All optimizations and simulations were made with the *Netzsch* program. *Fig. 9* shows the comparison between experimental and simulated curves. The so obtained kinetic parameters are listed in *Table 3*.

Analogy between autocatalysis and first-order reaction: The temperature-programmed mode is the most commonly used method in thermoanalysis, but such *DSC* curves are difficult to simulate compared to the isothermal ones, because the reactant concentration and the rate constants are both a function of time and of temperature. The dependence of the rate constants on the temperature is given by the *Arrhenius* equation:

$$k(T) = a \exp\left(\frac{-E_a}{RT}\right) \tag{28}$$

To estimate the reactant concentration, the integrated form of *Eqn. 28* is needed:

$$I(T) = a\int \exp\left(\frac{-E_a}{RT}\right) dT \tag{29}$$

However no algebraic solution of *Eqn. 29* can be found without simplifications [31]. If $E_a/RT >> 1$, a semi-convergent serie can be used to simplify this integral:

Table 2. *Estimates of Activation Energies and of Pre-exponential Using Methods 1 and 2*

	First method	Second method
initiation reaction		
E_{a1} [kJ/mol]	129.3	128.6
$\log_{10}(a_1)$ [s^{-1}]	8.8	8.6
autocatalytic reaction		
E_{a2} [kJ/mol]	132.2	133.6
$\log_{10}(a_2)$ [s^{-1}]	9.4	9.4

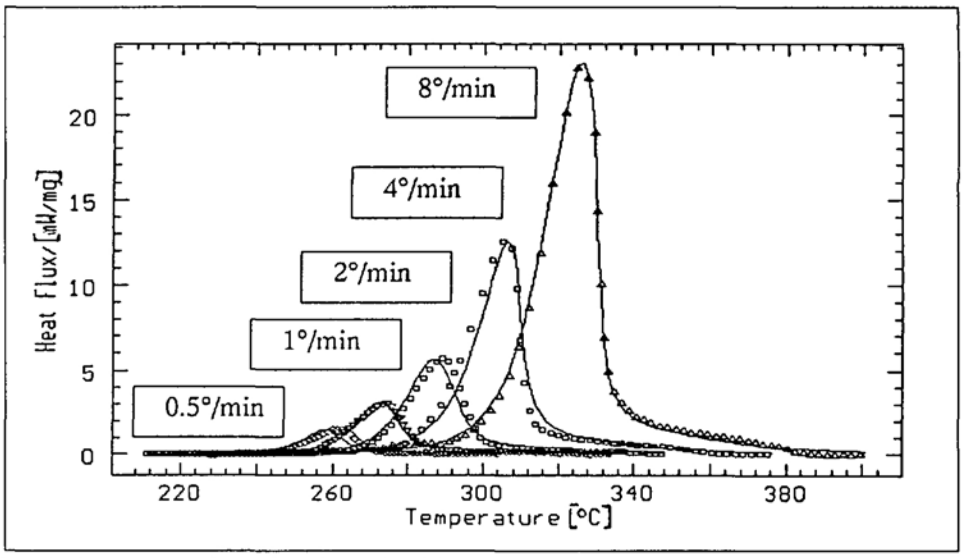

Fig. 9. *Experimental* (points) *and simulated* (lines) *DSC curves: temperature-programmed mode*

$$I(T) \approx -aT \exp\left(\frac{-E_a}{RT}\right)\sum_{i=1}^{i=n}\left((-1)^i i!\left(\frac{RT}{E_a}\right)^i\right) \tag{30}$$

Using the following substitution of variables:

$$\frac{d[A]}{dt} = \frac{dT}{dt}\frac{d[A]}{dT} = \beta\frac{d[A]}{dT} \tag{31}$$

where β is the heating rate, the reaction rate *r* of the autocatalysis can be written as follows:

$$r = -\beta \frac{d[A]}{dT} = k_1(T)\,[A] + k_2(T)\,[A]\,(1-[A]) \tag{32}$$

We assume the reactant concentration to be:

$$[A] = x(T)\exp\left(-\frac{1}{\beta}\,(I_1(T) + I_2(T))\right) \tag{33}$$

where $x(T)$ is an unknown function of the temperature. $I_1(T)$ and $I_2(T)$ correspond to the initiation and the catalysis reaction, respectively. $x(T)$ can be found by introducing *Eqn. 33* in *Eqn. 32*. The solution of this differential equation is as follows:

$$[A] = \frac{\exp\left(-\frac{1}{\beta}\,(I_1(T) + I_2(T))\right)}{1/[A]_0 - \frac{k_2}{\beta}\int_{T_0}^{T}\exp\left(-\frac{1}{\beta}\,(I_1(T) + I_2(T))\right)dT} \tag{34}$$

If $T \rightarrow T_0$, then $[A] \rightarrow [A]_{T\rightarrow T_0}$ ($[A]_{T_0} = [A]_0$) thus *Eqn. 34* becomes:

$$[A]_{T\rightarrow T_0} \approx [A]_0\exp\left(-\frac{1}{\beta}\,(I_1(T) + I_2(T))\right) \tag{35}$$

This expression (*Eqn. 35*) can be compared with the expression found for a first-order reaction under the temperature-programmed mode:

$$[A] = [A]_0\exp\left(-\frac{1}{\beta}\,k\,(T_0 - T)\right) \tag{36}$$

where the exponential of *Eqn. 35* contains the activation energies of the initiation and the catalysis reactions. That is the reason why a single experimental *DSC* curve of an autocatalytic reaction can be modeled by a model of first order reaction with a very high value of the activation energy (*Fig. 10* and *Table 3*).

Table 3. *Estimates of Activation Energies and Pre-exponential Factors Using the Temperature Programmed Mode*

	Initiation reaction	Autocatalytic reaction	First-order reaction
Activation energy	128.8 kJ/mol	132.6 kJ/mol	346.2 kJ/mol
Pre-exponential factor $\log_{10}(a_i)$	8.8	9.4	12.3

6. Modelling the Adiabatic Case

Adiabatic conditions are realized when no heat exchange between the reaction mixture and the surroundings takes place. When a cooling failure occurs, the effectiveness of the cooling system is suddenly reduced to very low values. Hence, adiabacity is a good approximation for the heat balance after a cooling failure has occurred.

The increase in temperature can be written as:

$$\Delta T_{ad} = T_f - T_i = (-\Delta H_r)/c_p \tag{37}$$

and the conversion becomes:

$$\alpha = (T - T_i)/\Delta T_{ad} \tag{38}$$

The single variable is the temperature which is a function of time. According to *Eqns. 1*, *3*, *37*, and *38*:

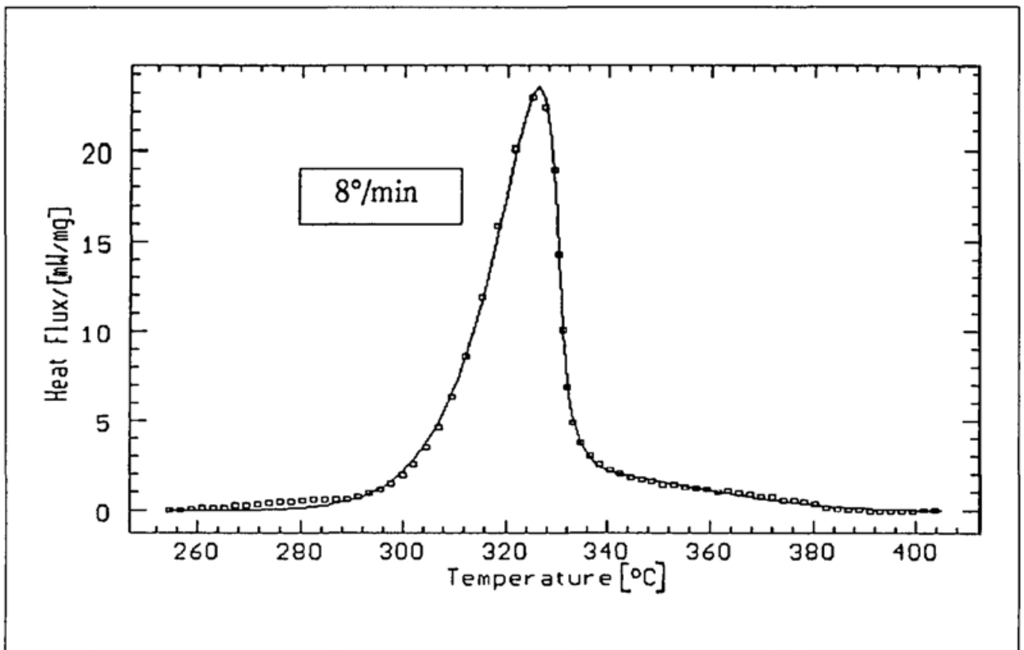

Fig. 10. *Experimental* (points) *and simulated* (line) *DSC curves using a model of first order with the temperature-programmed mode*

CHIMIA 48 (1994) Nr. 12 (Dezember)

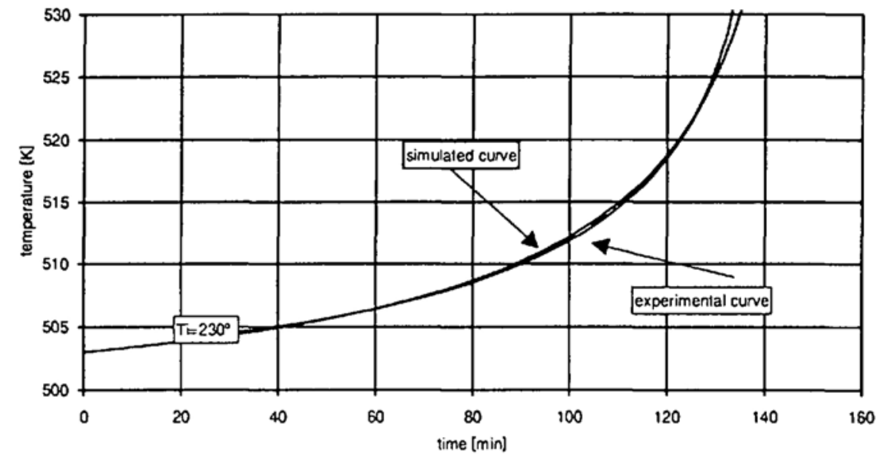

Fig. 11. *Experimental and simulated ARC curves: 'heat, wait, and search' mode*

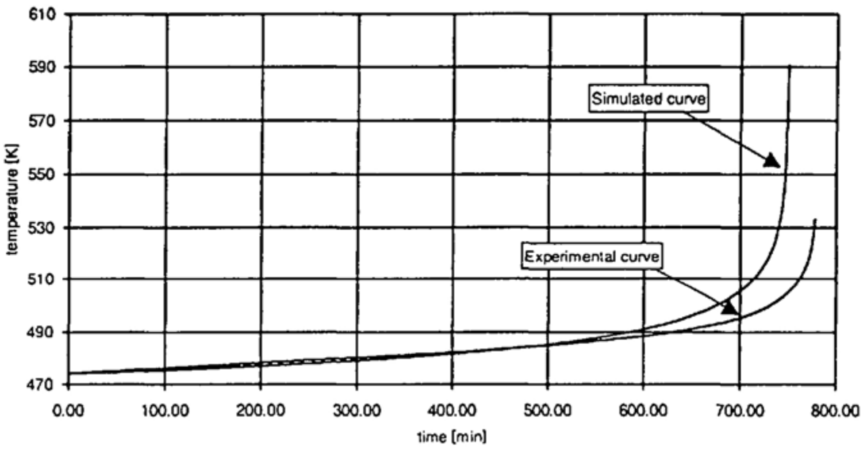

Fig. 12. *Experimental and simulated ARC curves: 'isothermal age' mode*

$$\frac{dT}{dt} = (T_f - T)\left(k_1(T) + [A]_0\ k_2(T)\ \frac{T - T_i}{\Delta T_{ad}}\right) \quad (39)$$

with $k_1(T) = a_1 \exp(-E_{a1}/RT)$ and $k_2(T) = a_2 \exp(-E_{a2}/RT)$.

No analytical solution of this equation was found. *Eqn. 39* was solved numerically.

The simulation parameters were chosen in such a way that always slightly shorter times than in reality were obtained (*Figs. 11* and *12*).

The corresponding results are shown in *Table 4*.

Thus, the adiabatic case can be well modelled using isothermal measurements, as can be seen from a comparison of *Tables 2* and *4*. Simulations with errors of ±1% in E_{a1} and E_{a2} give a scatter of values for the TMR_{ad} in a range of 15% around the true value.

Table 4. *Estimates of Activation Energies from ARC-experiments*

	Heat-wait-search mode	'Isothermal age' mode
Initiation reaction E_{a1} [kJ/mol]	128.9	129.2
Autocatalytic reaction E_{a2} [kJ/mol]	129.6	132.2

7. Conclusion

It has been shown that the adiabatic behavior of autocatalytic decompositions can be described using kinetic parameters deduced from isothermal *DSC* curves. The second method presented is easy to apply, reliable, and takes very little time. Experience within our company shows that de-

CHIMIA 48 (1994) Nr. 12 (Dezember)

composition reactions of many nitro compounds can be treated in the same way. Compared to a simplified zero-order approximation the time to explosion is increased by a factor of 10 depending on the nature of the substance, *i.e.*, on the kinetic parameters. This allows to work at higher temperatures without increasing the risk of a runaway. This result can be achieved due to a more comprehensive knowledge of the decomposition kinetics.

This work is a part of the PhD thesis prepared by *J.M. Dien* at the 'Université de Haute-Alsace' (Mulhouse) with the financial support of the *Research Services Physics* and of the *Corporate Unit Safety and Environnement* of *Ciba* (Basel).

Received: July 11, 1994

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List of symbols

TMR_{ad}:	time to maximum rate under adiabatic conditions	[s]
[A]:	concentration of reactant A	[mol/kg]
$[A]_0$:	initial concentration of reactant A	[mol/kg]
[B]:	concentration of catalyst B	[mol/kg]
$[B]_0$:	initial concentration of catalyst B	[mol/kg]
a_1:	pre-exponential factor for the initiation reaction	[s^{-1}]
a_2:	pre-exponential factor for the autocatalytic reaction	[$kg \cdot mol^{-1} \cdot s^{-1}$]
k_1:	rate constant of the initial reaction	[s^{-1}]
k_2:	rate constant of the autocatalytic reaction	[$kg \cdot mol^{-1} \cdot s^{-1}$]
E_{a1}:	activation energy of the initial reaction	[kJ/mol]
E_{a2}:	activation energy of the autocatalytic reaction	[kJ/mol]
$-\Delta H_r$:	total reaction enthalpy	[J/g]
$-\Delta H_t$:	partial reaction enthalpy until the time t	[J/g]
t:	time	[s]
T:	temperature	[K]
T_{ad}:	temperature increase under adiabatic conditions	[K]
T_i:	initial temperature	[K]
T_f:	final temperature	[K]
c_p:	specific heat capacity at constant pressure	[$J \cdot kg^{-1} \cdot K^{-1}$]
R:	ideal gas constant	[$J \cdot mol^{-1} \cdot K^{-1}$]
q:	heat release rate	[W/kg]
q_0:	heat release rate at the temperature T_i	[W/kg]
q_{ref1}:	heat release rate at the beginning	[W/kg]
q_{ref2}:	heat release rate at the maximum	[W/kg]
α:	conversion	
α_0:	degree of autocatalysis	
r:	reaction rate	
i:	stoichiometric coefficient of substance i	
a, b, c:	reaction orders	
$I(T)$:	*Arrhenius* integral	

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