

# Prediction of Self-Reactive Properties from DTA-Measurements

Prof. Dr. Jörg Steinbach \*, Technische Universität Berlin Germany

Dr. Odo Klais, Hoechst AG Frankfurt a.M. Germany

The Rio conference proposed a harmonised classification system which is based on the common classification system for the transport of dangerous goods regarding physico-chemical properties. The UN-Committee of Experts on the transport of dangerous goods recommends test procedures for the identification, classification and labelling. In spite of their general acceptance the tests and their procedures are regarded as quite costly. Therefore industry is interested to enhance the use of reliable screening procedures to avoid unnecessary testing. Subject of endless discussions however is the fixing of criteria, which allow to discriminate between substances to be exposed to intensified testing and such to be excluded from the recommended procedures.

For UN-Class 4, Div. 4.1 „Self-Reactive Substances“ a systematic investigation was performed in order to develop reliable criteria for the interpretation of standard DTA - test results. For this purpose heat accumulation storage tests were simulated based on normal n-th order as well as on autocatalytic kinetic rate laws. This way relevant kinetic parameter combinations of self-reactive substances were identified. Subsequently these were used to simulate the corresponding DTA-test. The DTA-test results were characterised as commonly done by onsets and other safety relevant data. Parallel to these activities models were developed successfully, which relate those DTA-data to characteristic heat accumulation storage test data, such as SADT and adiabatic induction times. Model development was mainly based on the well known explosion theory and standard scale-up rules.

Having identified the border line, which separates substances with possible self-reactive kinetic characteristics from non-self-reactives, the models will allow the prediction of possible self-reactive properties from common DTA-test results.

## Introduction

The existing testing scheme, which has to be applied to determine transport package sort, size and conditions as well as the necessary labelling for UN-Class 4, Div. 4.1 „Self-Reactive Substances“, prescribes rather extensive test methods. Therefore it is understandable that many are hoping for criteria to interpret simpler screening test results applied at an earlier stage to discriminate potentially self-reactive and non-self-reactive substances. This would reduce costly testing efforts remarkably.

Industrial practice has proven that DTA/DSC or tests with comparable measuring principle are suitable screening techniques to identify such potential. But it turns out to be critical nonetheless detrimental to be able to agree upon criteria, which allow for a reliable exclusion of only those substances, which are truly non-self-reactive.

With the help of a parameter study and dynamic simulation techniques for the relevant test methods it was attempted to backup or to adjust empirical exclusion criteria by a scientifically sound theory. Practical experience says:

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\* author to whom correspondence should be sent to

TU Berlin, IPAT-Process Safety and Technology - BU-B2, Budapest Str. 48, D 10787 Berlin  
Phone: +49-30-314 26 929, Fax : +49-30-314 26 907, e-mail: stein@dynamik.fb10.tu-berlin.de

- if the onset temperature of decomposition measured in a DTA using a heating rate of 3 to 5 K/min is greater than 175°C

or

- if the heat of decomposition is less than 1-3001 KJ/Kg

the substance does not have self-reactive properties.

## General Procedure

The *UN-Recommendations On The Transport Of Dangerous Goods* recommend among others a limit value of 75°C for the SADT to discriminate between self-reactive and non-self-reactive substances. Therefore the SADT is selected as the characteristic property for comparative purposes. One possibility to determine the SADT is the use of the heat accumulation storage test. In accordance with the UN recommendations its value is defined as the lowest initial temperature at which under strictly defined storage conditions a runaway can be observed within seven days. At the same time it is required, that no remarkable temperature increase may be observed within these seven days, if the initial temperature was lowered by 10 K.

The questions to be answered consecutively are now:

1. Which parameter combinations do fulfil the condition  $SADT = 75\text{ °C}$  with an induction time of no more than  $\tau_{ad} = 7$  days assuming different kinetic rate laws?
2. Are there any parameter combinations among those identified under 1, which have a heat of decomposition of less than 1-3001 KJ/Kg or a smaller adiabatic temperature increase  $\Delta T_{ad}$  than 150 K?
3. What is the DTA-pattern for substances represented by the identified kinetic and thermodynamic parameter combinations?
4. Do the simulated DTA-results support an onset criterion as proposed by industry of greater than 175°C for non-self-reactive substances?

With respect to the kinetic expressions used in this study, n-th order rate laws with a focus on  $n = 1$  and Prout-Tomkins autocatalytic reactions were considered. This can be justified by the fact, that reactions with  $n > 1$  proceed at comparatively lower rates. The majority of self-reactive substances show a more or less autocatalytic decomposition behaviour. The Prout-Tomkins rate law allows for sufficient variability to cover most of the relevant decomposition patterns.

## Decomposition Reactions with 1-Order Rate Law

The heat accumulation storage test may be modelled by an adiabatic batch-reactor. The related heat balance assuming a first order decomposition reaction has the following form:

$$\frac{dT}{dt} = \Delta T_{ad} \cdot k_{\infty} \cdot \left(1 - \frac{T - T_0}{\Delta T_{ad}}\right) \cdot e^{-\frac{E}{R \cdot T}}$$

This differential equation can numerically be solved, provided the activation energy  $E$  is known. The appropriate limits of integration are:

$t = 0$  and  $T(t=0) = 348.15 \text{ K } (75^{\circ}\text{C})$  as the initial condition

$t = \tau_{ad}$  and  $T(\tau_{ad}) = T\Big|_{\frac{dT}{dt}=\text{max}}$  as the upper limit.

The upper limit for the temperature variable can be obtained from the boundary condition:

$$\left. \frac{d^2T}{dt \cdot dT} \right|_{\frac{dT}{dt} \text{ MAX}} = 0 \quad \Leftrightarrow \quad T\Big|_{\tau_{ad}} = \frac{E}{2 \cdot R} \cdot \left( \sqrt{1 + 4 \cdot \frac{R}{E} \cdot (\Delta T_{ad} + T_0)} - 1 \right)$$

Separation of the variables yields:

$$k_{\infty} = \frac{1}{\tau_{ad} \cdot \Delta T_{ad}} \cdot \int_{T_0=348.15 \text{ K}}^{T(\tau_{ad})} \frac{1}{1 - \frac{T - T_0}{\Delta T_{ad}}} \cdot e^{\frac{E}{R \cdot T}} \cdot dT$$

If the activation energy  $E$  and the adiabatic temperature increase  $\Delta T_{ad}$  are varied now within physically reasonable limits the missing pre-exponential factor  $k_{\infty}$  can be determined as the last missing parameter.

The next step is to select those parameter combinations from the matrix obtained in the previous step, which also fulfil the second requirement of a SADT =  $75^{\circ}\text{C}$ . If the observable temperature increase was less than 5 K for an initial temperature of  $65^{\circ}\text{C}$  within the simulated storage time of 7 days it was assessed as non-remarkable. All those parameter combinations with a higher temperature increase at  $65^{\circ}\text{C}$  have SADTs of less than  $75^{\circ}\text{C}$  and should be regarded as self-reactive. An example plot of a heat accumulation storage test simulation for a SADT =  $75^{\circ}\text{C}$  parameter set is shown in Fig. 1.

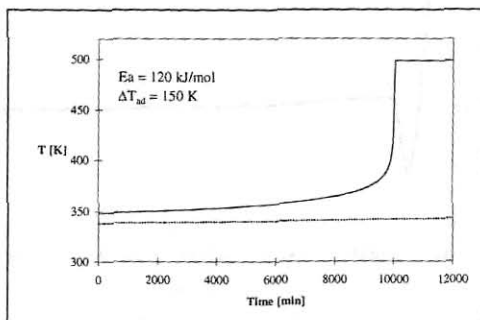


Fig. 1: Example for simulated temperature time profiles of a Heat Accumulation Storage Test - SADT =  $75^{\circ}\text{C}$  - dotted line:  $T_0 = 65^{\circ}\text{C}$

The result of this identification process is shown in Table 1. The curiosity observed with reactions, which have an adiabatic temperature increase of  $\Delta T_{ad} = 25$  K, is not of any subject to this presentation. As a first evaluation it may be stated, that non-autocatalytic decomposing self-reactive substances have activation energies of less than  $E < 100$  KJ/mol and this - in first approximation - independent of the related adiabatic temperature increase (c.f. Fig. 2).

		$E_A$ [kJ/mol]							
		40.00	48.00	56.00	64.00	80.00	100.00	120.00	160.00
$\Delta T_{ad}$	10								
	25								
koo [min <sup>-1</sup> ]	10								
k (75°C) [min <sup>-1</sup> ]	10								
koo [min <sup>-1</sup> ]	25			102.3	2090	6.51E+05	6.90E+08	6.65E+11	5.56E+17
k (75°C) [min <sup>-1</sup> ]	25			4.0515E-07	5.2188E-07	6.4648E-07	6.8323E-07	6.5803E-07	5.48202E-07
koo [min <sup>-1</sup> ]	35							5.31E+11	3.98E+17
k (75°C) [min <sup>-1</sup> ]	35							5.2552E-07	3.9253E-07
koo [min <sup>-1</sup> ]	50							3.72E+11	2.624E+17
k (75°C) [min <sup>-1</sup> ]	50							3.6788E-07	2.58534E-07
koo [min <sup>-1</sup> ]	100							1.66E+11	1.19E+17
k (75°C) [min <sup>-1</sup> ]	100							1.6377E-07	1.16853E-07
koo [min <sup>-1</sup> ]	150							1.057E+11	7.686E+16
k (75°C) [min <sup>-1</sup> ]	150							1.0453E-07	7.57276E-08
koo [min <sup>-1</sup> ]	300							5.089E+10	3.745E+16
k (75°C) [min <sup>-1</sup> ]	300							5.0327E-08	3.68982E-08

Table 1: Parameter combinations  $E$ ,  $k_{oo}$ , and  $\Delta T_{ad}$ , which result in a SADT = 75 °C determined in the heat accumulation storage test.

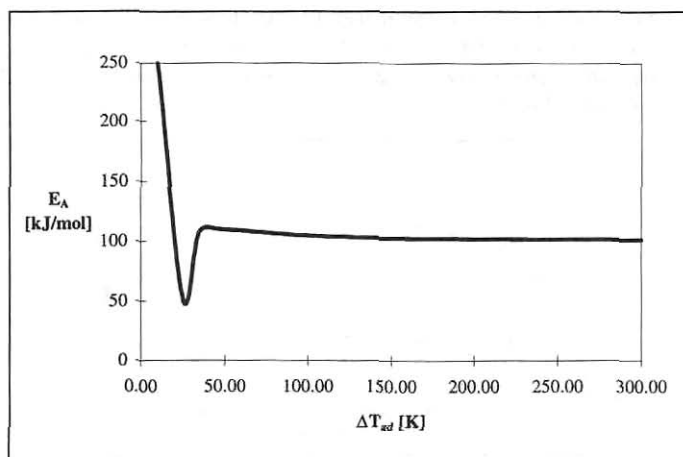


Fig. 2: Borderline for SADT = 75°C, reaction order  $n = 1$

## Pre-calculation of Corresponding DTA-Onsets

The pre-calculation of corresponding DTA-onsets of scanning experiments with heating rates of 3-5 K/min is based on the well known explosion theory of Semenov. One of the core statements of the explosion theory is, that a runaway will always occur,

- if the balance of heat removal and heat production is lost in favour of the heat production rate
- and if the temperature gradient of the heat production rate always exceeds the gradient of the heat loss rate once the temperature has increased beyond the equilibrium temperature.

The equation, which describes the state of critical balance between heat production and removal rate for a 0.-order reaction, is:

$$\frac{1}{e} = \frac{k'(T) \cdot E \cdot \Delta T_{ad} \cdot V \cdot \rho \cdot c_p}{U \cdot A \cdot R \cdot T^2}$$

This formulation assumes, that the temperature dependence of the rate constant can be described with by the Arrhenius relationship. The pre-calculation now assumes, that the DTA-onset as well as the SADT correspond to this first deviation from the equilibrium state. Consequently the ratio of the two equilibrium state equations is calculated.

$$\frac{T_{DTA}^2}{\exp\left(-\frac{E}{R \cdot T_{DTA}}\right)} = \frac{T_{HAST}^2 \cdot V_{DTA} \cdot U_{HAST} \cdot A_{HAST}}{\exp\left(-\frac{E}{R \cdot T_{HAST}}\right) \cdot V_{HAST} \cdot U_{DTA} \cdot A_{DTA}}$$

As a first approximation an identical overall heat-transfer coefficient is assumed for both measuring systems. The same shall hold true for the geometric factors of the two different sample containers.

$$\frac{\text{Height}}{\text{Diameter}}; \quad \frac{H}{D} = \frac{H}{2 \cdot r} = 2$$

With these assumptions rearrangement yields an equation, which describes the correlation between the two critical equilibrium temperatures. The parameters are the activation energy and the mass scale-factor.

$$1 = \exp\left(\frac{E}{R} \cdot \left(\frac{1}{T_{HAST}} - \frac{1}{T_{DTA}}\right)\right) \cdot \left(\frac{T_{HAST}}{T_{DTA}}\right)^2 \cdot \sqrt[3]{\frac{m_{DTA}}{m_{HAST}}}$$

Inserting the parameter combinations identified for the heat accumulation storage test the corresponding DTA-onsets can be estimated. The corresponding heat production rates can be calculated according to

$$\dot{Q}_{DTA} = \dot{Q}_{HAST} \cdot \left( \frac{m_{DTA}}{m_{HAST}} \right) \cdot \exp\left(-\frac{E}{R} \cdot \left( \frac{1}{T_{DTA}} - \frac{1}{T_{HAST}} \right)\right)$$

The results must be independent of  $\Delta T_{ad}$ . Figure 3 shows the general dependence of the modelled  $T_{DTA}$  on the activation energy.

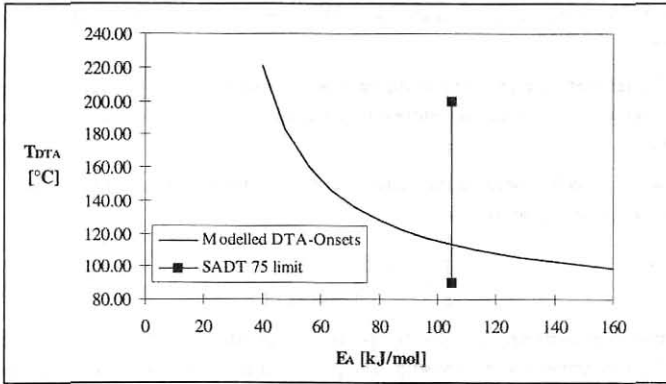


Fig. 3: Modelled T-onset for first order reactions with a SADT  $\approx 75^\circ\text{C}$  determined in a Heat Accumulation Storage Test

As can be seen, the modelled values for  $T_{DTA}$  are considerably lower than the proposed limit of  $175^\circ\text{C}$  for the exclusion of non-self-reactive substances, if the activation energy is greater than  $50\text{ kJ/mol}$ .

### Validation of the Pre-calculated T-onset Values

The model must be validated with the help of exact values for DTA-onsets obtained from simulated DTA thermograms. The comparison of modelled and simulated onsets will indicate the reliability of the predictions. Examples are given in the following figures. Figure 4 shows simulated thermograms for parameter combinations with fixed values for  $\Delta T_{ad} = 150\text{ K}$  and  $\tau_{ad} = 7$  days, Figure 5 for parameter combinations with fixed values for  $E = 160\text{ KJ/mol}$ . For those simulations a heating rate of  $5\text{ K/min}$  was chosen as lower heating rates would shift the observable effects to lower temperatures. As observable onset a heat output of  $0.0001\text{ W}$ , which corresponds to a threshold of  $5\text{ mW/g}$ , was chosen.

In order to improve the determination of the onset temperatures a blow-up of the power range close to  $0.0001\text{ W}$  is additionally shown.

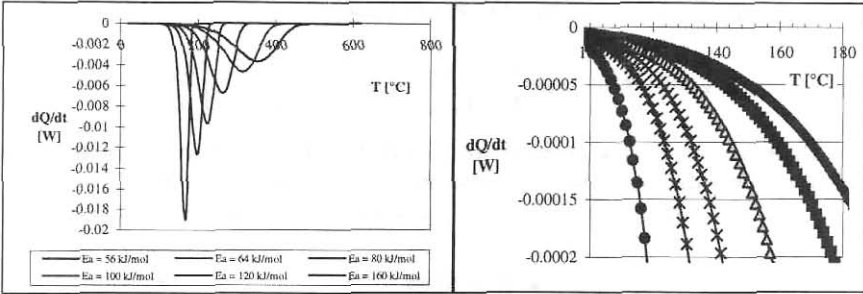


Fig. 4: Simulated DTA-Thermograms for reactions of first order kinetics and  $\Delta T_{ad} = 150 \text{ K}$  ( for  $E = 120$  and  $160 \text{ KJ/mol}$  the SADT is greater than  $75^\circ\text{C}$  )

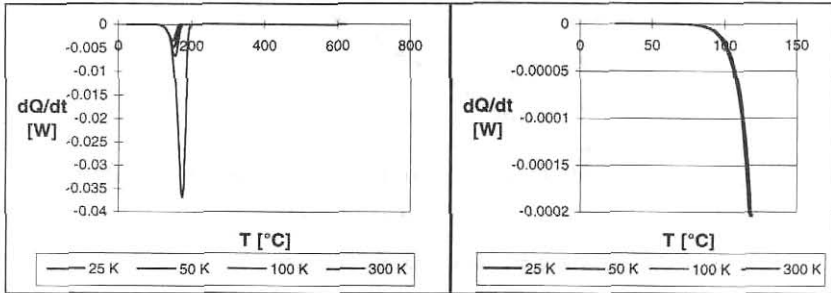


Abb. 5: Simulated DTA-Thermograms for reactions of first order kinetics and  $E = 160 \text{ KJ/mol}$  (for all  $\Delta T_{ad}$  -values the SADT is greater than  $75^\circ\text{C}$ )

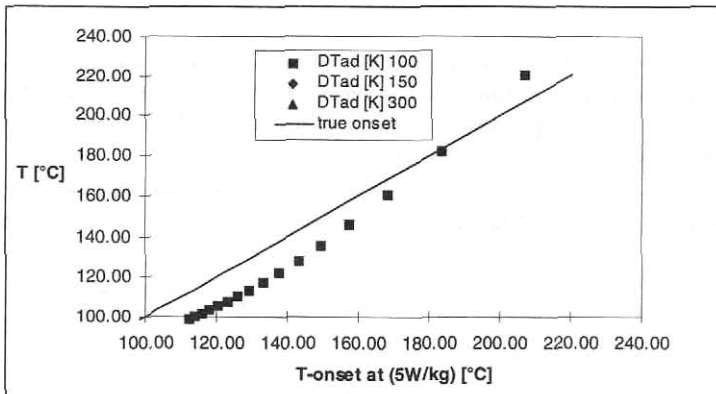


Fig. 6: Comparison of pre-calculated and simulated DTA T-onset

Figure 6 shows the comparison of pre-calculated and simulated T-onsets. For first order reactions the model may be regarded as reasonably applicable. A minor correction should enable a predictions with the necessary accuracy.

The extended correlation is presented in the next equation

$$I = 0.00345 \cdot E^{1.48} \exp\left(\frac{E}{R} \cdot \left(\frac{1}{T_{\text{HAST}}} - \frac{1}{T_{\text{DTA}}}\right)\right) \cdot \left(\frac{T_{\text{HAST}}}{T_{\text{DTA}}}\right)^2 \cdot \sqrt[3]{\frac{m_{\text{DTA}}}{m_{\text{HAST}}}}$$

With the help of this final model equation a prediction of the observable DTA- onsets and vice versa of the SADT is possible now with surprising accuracy as shown in Fig. 7.

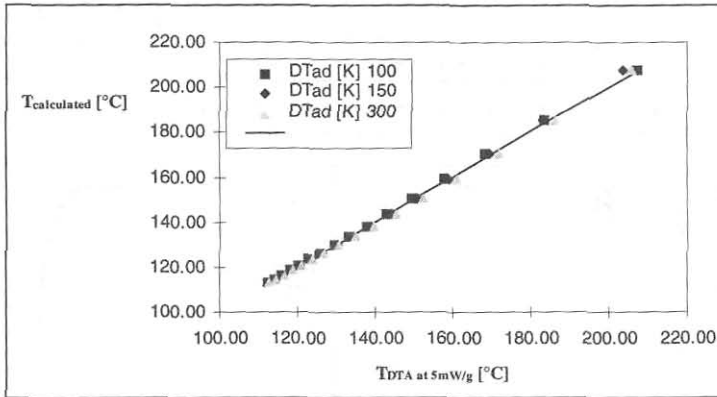


Fig. 7: Comparison of pre-calculated and simulated DTA T-onset

## Decomposition Reactions with Autocatalytic Rate Law

A great number of decomposition reactions follow autocatalytic kinetic rate laws. Their complex phenomenology, e.g. long induction times followed by extreme steep self-heat rates, leads to a greater number of parameters needed in modelling. Therefore, this paper can cover only a limited selection of the parameter ranges possible.

The Prout-Tompkin rate law has proven its suitability for the description of many autocatalytic decomposition reactions. The investigation shall be exemplified for the following model:

$$\frac{dT}{dt} = \Delta T_{\text{ad}} \cdot k_{\infty} \cdot \left(1 - \frac{T - T_0}{\Delta T_{\text{ad}}}\right) \cdot \left(1 + P(T) \cdot \frac{T - T_0}{\Delta T_{\text{ad}}}\right) \cdot \exp\left(-\frac{E_0}{R \cdot T}\right)$$

with

$$P(T) = \frac{k_{\text{auto}} \cdot c_{A0}}{k_0} = \frac{k_{\text{oo,auto}} \cdot c_{A0} \cdot \exp\left(-\frac{E_{\text{auto}}}{R \cdot T}\right)}{k_{\text{oo},0} \cdot \exp\left(-\frac{E_0}{R \cdot T}\right)} = P_{00} \cdot \exp\left(-\frac{(E_{\text{auto}} - E_0)}{R \cdot T}\right)$$



The indices „0“ and „auto“ refer to the initialising and the accelerating reaction, respectively. This adiabatic heat balance of a batch process can numerically be integrated, if  $E_0$ ,  $E_{\text{auto}}$ , and  $P_{00}$  are given. The appropriate limits of integration are:

$$\begin{aligned}
 t = 0 \text{ and } T(t=0) &= 348.15 \text{ K (75}^\circ\text{C)} && \text{the initial condition} \\
 t = \tau_{\text{ad}} \text{ and } T(\tau_{\text{ad}}) &= T \Big|_{\frac{dT}{dt} = \text{max}} && \text{the upper limit.}
 \end{aligned}$$

Again, the upper limit for the temperature variable can be obtained from the boundary condition:

$$\frac{d^2 T}{dt \cdot dT} \Big|_{\frac{dT}{dt} = \text{max}} = 0$$

In this case, however, the resulting equation can only be solved iteratively.

$$1 - \left( 1 - \frac{T - T_0}{\Delta T_{\text{ad}}} \right) \cdot \frac{E_0 \cdot \Delta T_{\text{ad}}}{R \cdot T^2} = \frac{\left( 1 - \frac{T - T_0}{\Delta T_{\text{ad}}} \right)}{\left( 1 + P(T) \cdot \frac{T - T_0}{\Delta T_{\text{ad}}} \right)} \cdot P(T) \cdot \left[ \frac{T - T_0}{\Delta T_{\text{ad}}} \cdot \frac{(E_{\text{auto}} - E_0) \cdot \Delta T_{\text{ad}}}{R \cdot T^2} - 1 \right]$$

For known values of  $E_0$ ,  $E_{\text{auto}}$ ,  $\Delta T_{\text{ad}}$  and  $P$ , the corresponding value for  $k_{00}$ , which fulfils the boundary condition of  $\tau_{\text{ad}} = 7$  days, can be determined from the rearranged heat balance:

$$k_{\infty,0} = \frac{1}{\tau_{\text{ad}} \cdot \Delta T_{\text{ad}}} \cdot \int_{T_0=348.15 \text{ K}}^{T(\tau_{\text{ad}})} \frac{1}{\left( 1 - \frac{T - T_0}{\Delta T_{\text{ad}}} \right) \cdot \left( 1 + P_{00} \cdot e^{-\frac{(E_{\text{auto}} - E_0)}{R \cdot T}} \cdot \frac{T - T_0}{\Delta T_{\text{ad}}} \right)} \cdot e^{\frac{E_0}{R \cdot T}} \cdot dT$$

As an example only those parameter combination shall be evaluated here, which are obtained for  $\Delta T_{\text{ad}} = 150 \text{ K}$  and  $P = 5$ . As an example the temperature profiles obtained in a Heat Accumulation Storage Test are given in Figure 8.

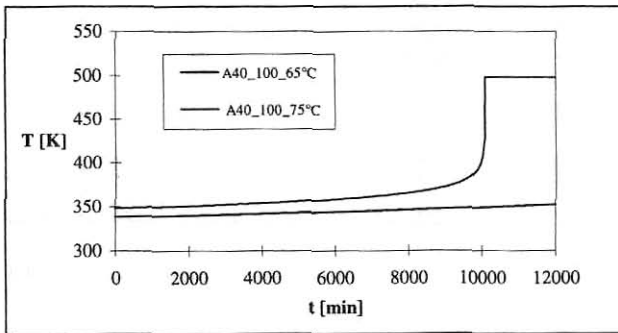


Fig. 8: Simulated temperature profiles obtained in a Heat Accumulation Storage Test  $E_0 = 40 \text{ KJ/mol}$ ,  $E_{\text{auto}} = 100 \text{ KJ/mol}$ ,  $\Delta T_{\text{ad}} = 150 \text{ K}$

**Pre-calculation of Corresponding DTA-Onsets**

The pre-calculation of the corresponding T-onset is basically founded on the same model, which was used for n-th order reactions. In the case of autocatalytic reactions the initial reaction rate depends not only on the initiating but also on the catalysing reaction. This has to be considered by accounting for the ratio  $P(T_{HAST})$  to  $P(T_{DTA})$  in an appropriate way. The following formulation turned out to be a good first approximation:

$$I = \exp\left(\frac{E}{R} \cdot \left(\frac{1}{T_{HAST}} - \frac{1}{T_{DTA}}\right)\right) \cdot \left(\frac{T_{HAST}}{T_{DTA}}\right)^2 \cdot \sqrt{\frac{m_{DTA}}{m_{HAST}}} \cdot \frac{\left(1 + 0.001 \cdot P_{\infty} \cdot e^{-(E_{auto} - E_0)/RT_{DTA}}\right)}{\left(1 + 0.001 \cdot P_{\infty} \cdot e^{-(E_{auto} - E_0)/RT_{HAST}}\right)}$$

The results of the modelled T-onsets for the selected parameter set are presented in Table 5. Again most results are well below the suggested value of 175°C for the exclusion of non-self-reactive substances!

T <sub>i</sub> [K]	m <sub>2</sub> [kg]	m <sub>1</sub> [kg]	ΔT <sub>ad</sub> [K]	c <sub>p</sub> [J/kg K]										
348.15	0.00002	0.5	150	2000										
T <sub>HAST</sub> [°C]	Zielwert	E <sub>0</sub> [kJ/mol]	E/R [K]	k <sub>00</sub> [s <sup>-1</sup> ]	E <sub>auto</sub> [kJ/mol]	E/R <sub>auto</sub> [K]	P <sub>∞</sub>	dQ/dt <sub>0.05</sub> [W]	T <sub>DTA</sub> [K]	T <sub>DTA</sub> [°C]	dQ/dt <sub>DTA</sub> [W]			
75	1.0000	40	4811	1.8027E-01	60	7217	5.0093E+03	0.02694	490.53	217.38	6.1398E-05			
75	0.9998	40	4811	1.5184E-01	80	9622	5.0186E+06	0.02269	473.98	200.83	4.2342E-05			
75	0.9993	40	4811	1.3228E-01	100	12028	5.0279E+09	0.01977	447.76	174.61	2.5585E-05			
75	1.0000	40	4811	1.1815E-01	120	14433	5.0372E+12	0.01766	426.99	153.84	1.6432E-05			
75	1.0000	40	4811	1.0731E-01	140	16839	5.0466E+15	0.01604	412.46	139.31	1.1523E-05			
75	0.9991	40	4811	9.8665E-02	160	19245	5.0560E+18	0.01474	402.11	128.96	8.6345E-06			
75	1.0005	60	7217	1.3629E+02	80	9622	5.0093E+03	0.02033	425.17	152.02	1.0704E-04			
75	1.0004	60	7217	1.2112E+02	100	12028	5.0186E+06	0.01807	423.26	150.11	2.8164E-04			
75	1.0000	60	7217	1.0949E+02	120	14433	5.0279E+09	0.01633	418.14	144.99	5.6558E-04			
75	1.0000	60	7217	1.0030E+02	140	16839	5.0372E+12	0.01496	410.34	137.19	7.6364E-04			
75	1.0001	60	7217	9.2821E+01	160	19245	5.0466E+15	0.01385	402.43	129.28	8.0023E-04			
75	1.0000	80	9622	1.0965E+05	100	12028	5.0093E+03	0.01633	401.05	127.90	5.6049E-05			
75	1.0000	80	9622	1.0069E+05	120	14433	5.0186E+06	0.01499	400.54	127.39	1.1692E-04			
75	1.0003	80	9622	9.3215E+04	140	16839	5.0279E+09	0.01388	399.25	126.10	2.2895E-04			
75	1.0010	80	9622	8.6933E+04	160	19245	5.0372E+12	0.01294	396.72	123.57	3.7768E-04			
75	1.0002	100	12028	9.1837E+07	120	14433	5.0093E+03	0.01365	388.46	115.31	3.6869E-05			
75	1.0003	100	12028	8.1008E+07	140	16839	5.0186E+06	0.01280	388.25	115.10	6.6038E-05			
75	1.0000	100	12028	8.1040E+07	160	19245	5.0279E+09	0.01204	387.79	114.64	1.1688E-04			
75	1.0008	120	14433	7.9073E+10	140	16839	5.0093E+03	0.01173	380.71	107.56	2.7176E-05			
75	1.0000	120	14433	7.5195E+10	160	19245	5.0186E+06	0.01115	380.61	107.46	4.4015E-05			
75	1.0002	140	16839	6.9470E+13	160	19245	5.0093E+03	0.01029	375.47	102.32	2.1454E-05			

Table 5: Modelled T-onset for a Prout-Tompkin reaction with ΔT<sub>ad</sub> = 150 K, F = 5 and τ<sub>ad</sub> = 7 days

Graphically the result is shown in Fig.9.

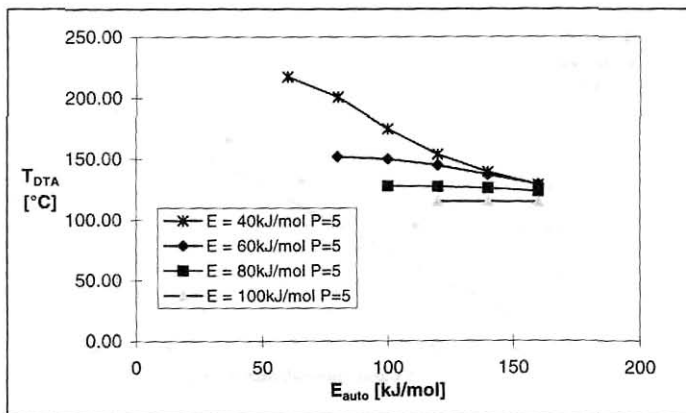


Fig. 9: Modelled T-onset for a Prout-Tompkin reaction with  $\Delta T_{ad} = 150$  K,  $P = 5$  and  $\tau_{ad} = 7$  days

### Validation of the Pre-calculated T-onset Values

Again, the model must be validated with the help of exact values for DTA-onsets obtained from simulated DTA thermograms. Examples are given in the following figures. Figure 9 shows simulated thermograms for parameter combinations with fixed values for  $\Delta T_{ad} = 150$  K and  $\tau_{ad} = 7$  days.  $E_0$  has a fixed value of 40 KJ/mol while  $E_{auto}$  is varied between 0 and 100 KJ/mol. This example was selected as the calculations predict the highest onset values. For those simulations a heating rate of 5 K/min was chosen as lower heating rates would shift the observable effects to lower temperatures. In order to improve the determination of the onset temperatures a blow-up of the power range close to 0.0001 Watt is additionally shown.

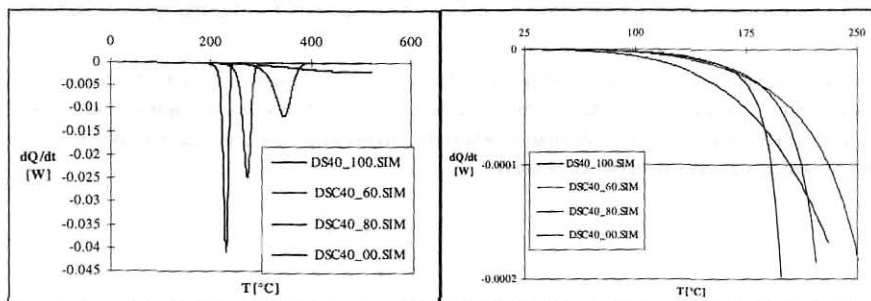


Fig. 10: Simulated DTA-Thermograms for autocatalytic reactions with  $\Delta T_{ad} = 150$  K,  $P = 5$

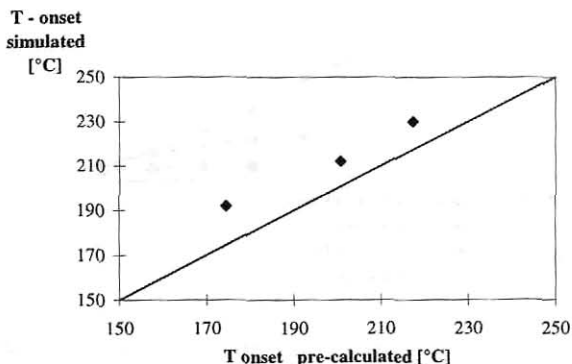


Fig. 11: Comparison of pre-calculated and simulated DTA T-onset for the autocatalytic case

The predictions do not have the same accuracy as those for n-th order reactions. But the underlying general trend provides an optimistic outlook for the ongoing work, to come up with another correlation for autocatalytic reactions.

## Conclusion

The results presented here provide an indication that it should be possible to derive correlations, which allow the safe prediction of the SADT from DTA scanning experiments for kinetically different decomposition reactions. For n-th order reactions the goal has already been achieved. The extension of this theory will provide a scientifically sound background for the implementation of screening test results in the recommendations for the transport of hazardous goods.

With respect to the proposed temperature limit of 175°C for non-selfreactive substances, the results show, that a moderate modification will be necessary up to value of approximately 200°C. A better defined limit will be available, when the investigation of autocatalytic processes will have reached a greater in depth knowledge.