# Application of DSC, advanced kinetic approach and heat balance for determination of thermal hazard

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## Introduction

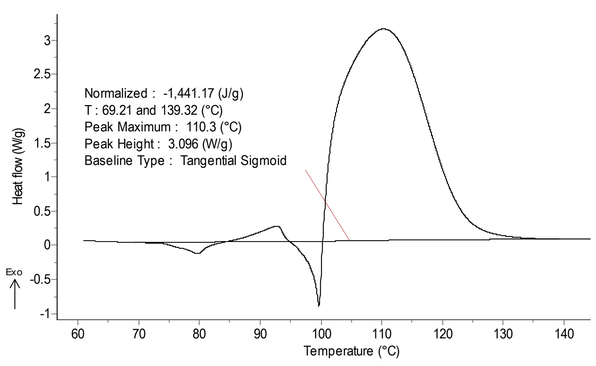
The methods of prediction of the thermal behavior of materials such as thermal hazard are strongly influenced by the sample mass. In mg-scale, all heat generated during exothermic reaction dissipates into surroundings, hence not influencing the temperature of the investigated sample. In large, ton-scale, when the systems can be treated as being almost adiabatic, the majority of the generated heat stays in the sample, which may lead to an uncontrolled temperature rise. In kg-scale, a very common and practical case, the temperature of the material results from the contributions of two processes differently dependent on temperature: heat generation and heat loss. On the contrary to heat dissipation, the generation of heat due to the exothermicity of the decomposition of the energetic material depends exponentially on temperature. As a consequence, the precise kinetic description of the process, depicting the heat generation rate and the exact heat balance in the investigated system, allows predicting correctly the thermal behavior of the energetic material. In the present study, the method of determination of the thermal hazard parameters from the mg-scale experiments was illustrated by the results obtained with Azobisisobutyronitrile (AIBN), CAS Number 78-67-1.

## Experimental

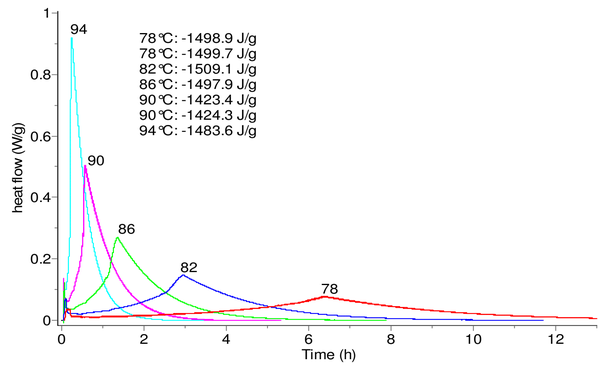
The kinetic parameters required for the simulation were calculated from the DSC traces, applying AKTS-Thermokinetics and AKTS-Thermal Safety Software [1]. The DSC experiments were carried out with a Mettler Toledo DSC 1 apparatus with pressure-resistant gold-plated sealed crucibles provided by Swissi PS Ltd. The preliminary experiment used for the determination of the temperature window in isothermal experiments was carried out with a heating rate of 2 K min$^{-1}$ 1.
The isothermal experiments were performed at temperatures lower than the detected melting range temperature. Seven runs 2 were performed isothermally (sample masses between 10.72 and 14.13 mg) at temperatures of 78, 82, 86, 90 and 94 °C, and measurements at 78 and 90 °C were repeated to check the reproducibility of the DSC traces. The thermal conductivity of AIBN was determined with the C-Therm TCi by Modified Transient Plane Source technique (C-Therm Technologies Ltd).

## Results

On DSC signal 1 before the exothermic decomposition the endothermic phase transition centred at ca. 80 °C is followed by melting at ca. 100 °C. Because the kinetic triplet determined for the decomposition in liquid state is inapplicable to predict the reaction rate in a solid state the isothermal DSC traces of AIBN were recorded at temperatures below melting. The mean value of the evolved heat, determined in all our experiments amounts to -1477 J g$^{-1}$ 2 and is also in very good agreement with the values of $\Delta H_r$ determined by means of static bomb calorimetry i.e. -1498 J g$^{-1}$ and -1394 J g$^{-1}$.




1 DSC traces of AIBN recorder by DSC at 2 K · min$^{-1}$



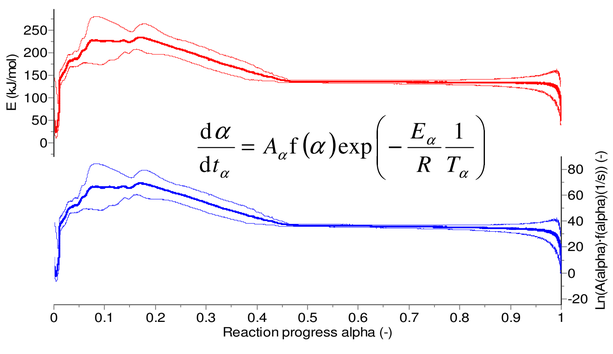

2 Heat flow traces of AIBN isothermal conditions

The mechanism of the decomposition of AIBN is not univocally specified in the literature therefore the kinetic parameters have been intentionally calculated by the differential isoconversional method. The logarithmic form of the reaction rate expression was applied for the calculation of E and A values at different degrees of conversion α without assuming the form of the function f(α):

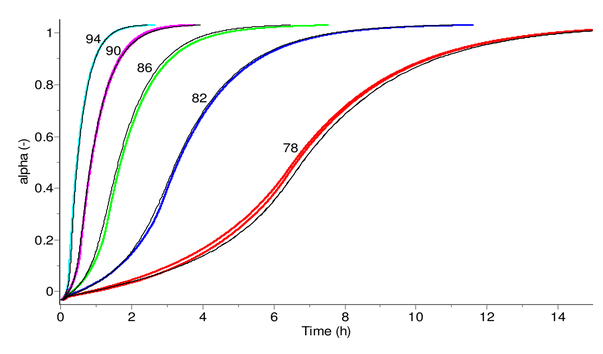
$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t_\alpha}\right) = \ln\{A_\alpha \mathrm{f}(\alpha)\} - \frac{E_\alpha}{R}\frac{1}{T_\alpha}$$

where $t_\alpha$, $T_\alpha$, $E_\alpha$ and $A_\alpha$ are the time, temperature, apparent activation energy and pre-exponential factor, at conversion α, respectively, and $-E_\alpha/R$ and $\ln\{A_\alpha f(\alpha)\}$ are the slope and the intercept with the vertical axis of the plot of $\ln(d\alpha/dt_\alpha)$ vs. $1/T_\alpha$. Having kinetic parameters characterizing the decomposition of AIBN in the solid state, it is then possible to the make kinetic predictions at any temperature profile T(t), from the values of $E_\alpha$ and $\{A_\alpha f(\alpha)\}$ extracted directly from the differential isoconversional method by the separation of the terms followed by an integration

$$t_\alpha = \int_0^{t_\alpha} \mathrm{d}t = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{\{A_\alpha \mathrm{f}(\alpha)\}\mathrm{e}^{-\frac{E_\alpha}{RT_\alpha}}}$$




3 Activation energy E (α) (bold) and {A (α)·$f$ (α)} (bold) of AIBN decomposition as a function of reaction progress α




4 Comparison of experimental and simulated (black) reaction progresses derived from the experimental DSC signals

The results of the determination of the kinetic parameters of AIBN decomposition 3 are presented in the form of the dependence of activation energy (left axis) and pre-exponential factor (right axis) on the reaction progress α. Next plot 4 depicts the experimental and simulated - by means of the determined kinetic parameters $E_\alpha$ and $\{A_\alpha f(\alpha)\}$ - dependences of the reaction progress α vs. time. The very good fit between the experimental traces and the simulated curves indicates the accuracy of the kinetic description of the process, something which cannot be obtained using simplified kinetic models of e.g. “first” order kinetics.

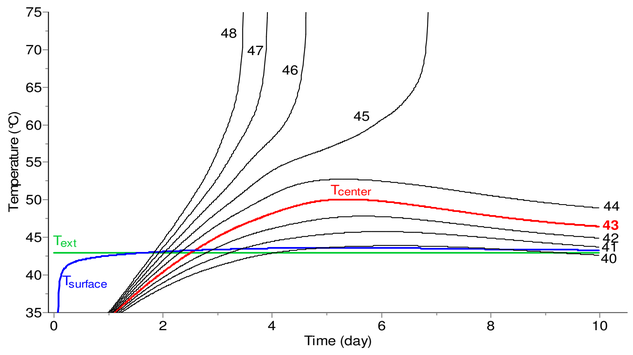
## Applying the kinetic parameters for the scale-up of thermal behaviour from mg- to kg-scale

During the DSC experiments carried out in mg-scale, all the heat generated during the exothermic reaction can be released from the sample and therefore does not influence the sample temperature in a noticeable extent. However, for larger sample masses during exothermal reactions, the rate of heat evolution may be greater than the rate of heat exchanged with the environment. It will result in heat accumulation in the sample, increasing its temperature in an uncontrolled way. Therefore, in the case of heat accumulation in the sample, the theory initially developed by Frank-Kamenetskii considering the heat balance in solid materials has to be considered. The following expressions describe the sample heating rate in mg 5 (as in DSC) and in kg scale 6 in which the $\Delta H_r$, $Cp$, $\lambda$, $\rho$, $g$ and $r$ mean: heat of reaction, specific heat, thermal conductivity, density, a geometry factor ($g$ = 0 for infinite plate, $g$ = 1 for infinite cylinder and $g$ = 2 for the sphere (as applied in this study)) and container radius, respectively.

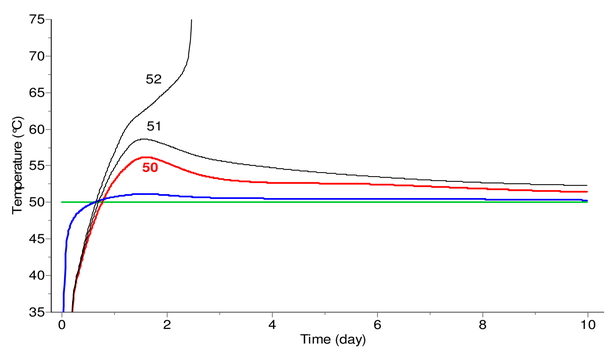
5 $$\frac{\mathrm{d}T}{\mathrm{d}t} = \beta \quad \begin{matrix}(\text{if } \beta > 0, \text{ non-isothermal})\\(\text{if } \beta = 0, \text{ isothermal})\end{matrix}$$

6 $$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{\lambda}{\rho\, Cp}\left(\frac{\partial^2 T}{\partial r^2} + \frac{g}{r}\frac{\partial T}{\partial r}\right) + \frac{-\Delta H_r}{Cp}\frac{\mathrm{d}\alpha}{\mathrm{d}t}$$

The thermal behavior of any, especially exothermically decomposed, material differs significantly in mg-, kg- or ton-scale not because of change of kinetic parameters of the decomposed substance (which are mass independent) but because of the heat exchange properties with the surrounding, being mass dependent.
Application of kinetic parameters 3 together with a heat balance 6 performed by numerical analysis allowed scale-up of thermal behavior of the sample from mg to kg scale. The results of the simulation of the SADT (Self Accelerating Decomposition Temperature) of AIBN are presented below for 50kg 7 and 5kg 8 samples. The simulated values of SADT of AIBN for various combinations of the overall heat transfer coefficient $U$ and sample mass $m$ using the criteria set in the United Nations SADT test H.1 are presented in Table 9.




7 Simulated thermal behavior of AIBN for mass of **50kg** with λ =0.072 W·m$^{-1}$·K$^{-1}$ and U = 5 W·m$^{-2}$·K$^{-1}$, respectively. SADT is marked in red.




8 Simulated thermal behavior of AIBN for mass of **5kg** with λ =0.072 W·m$^{-1}$·K$^{-1}$ and U = 5 W ·m$^{-2}$·K$^{-1}$, respectively. SADT is marked in red.

| Overall heat transfer coefficient $U$ / W m$^{-2}$ K$^{-1}$ | Sample mass $m$ / kg | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 500 | 200 | 100 | 50 | 20 | 10 | 5 | 2 | 1 | 0.5 | 0.4 | 0.3 | 0.2 | 0.1 |
| 10 | 37 | 38 | 41 | 43 | 46 | 49 | 51 | 54 | 56 | 59 | 60 | 60 | 60 | 61 |
| 5 | 37 | 38 | 40 | 43 | 46 | 48 | 50 | 53 | 56 | 58 | 58 | 59 | 60 | 60 |
| 2 | 37 | 38 | 40 | 42 | 45 | 47 | 49 | 52 | 54 | 55 | 56 | 57 | 58 | 59 |
| 1 | 37 | 37 | 39 | 41 | 43 | 45 | 47 | 50 | 51 | 53 | 53 | 54 | 55 | 56 |
| 0.5 | 37 | 37 | 38 | 39 | 42 | 43 | 45 | 47 | 48 | 50 | 50 | 51 | 52 | 53 |
| 0.4 | 37 | 37 | 38 | 39 | 41 | 42 | 44 | 46 | 47 | 49 | 49 | 50 | 51 | 52 |
| 0.3 | 37 | 37 | 38 | 39 | 40 | 41 | 43 | 45 | 46 | 47 | 48 | 48 | 49 | 50 |
| 0.2 | 37 | 38 | 38 | 38 | 39 | 40 | 41 | 43 | 44 | 45 | 46 | 46 | 47 | 48 |
| 0.1 | 38 | 38 | 38 | 39 | 39 | 39 | 39 | 40 | 41 | 42 | 42 | 43 | 44 | 45 |
| 0.05 | 39 | 39 | 39 | 39 | 39 | 39 | 39 | 39 | 39 | 40 | 40 | 40 | 40 | 41 |

9 Dependence of the SADT (°C) for AIBN on the overall heat transfer coefficient U (W·m$^{-2}$·K$^{-1}$) and the sample mass

The data depicted in Tab. 9 show quantitatively the influence of the overall heat transfer coefficient U on the SADT value. The 100-fold decrease of the mass from 50 to 0.5 kg results in the decrease of the SADT values (for U = 5 and 0.05 W m$^{-2}$ K$^{-1}$) from 43 °C to 39 °C and from 58 °C to 40 °C, respectively.

## Conclusions

The kinetics of decomposition of AIBN in the solid state was investigated in a narrow temperature window of 78-94 °C, just below the sample melting. The kinetic parameters of the decomposition were evaluated by differential isoconversional method. The very good fit of the experimental results with the simulation curves based on the determined kinetic parameters, indicated the accuracy of the kinetic description of the process. Application of the kinetic parameters, together with the heat balance performed by numerical analysis, allowed scale-up of the thermal behaviour and simulation of SADT. SADT values for AIBN obtained in this study (see also [2]) and those presented for other materials [3] indicate that software-based calculations with the correct kinetic approach and appropriate heat balance allow the successful scale-up of thermal behaviour from mg- to kg scale.

## References

1. AKTS-Thermokinetics and AKTS-Thermal Safety Software, http://www.akts.com
2. B. Roduit , M. Hartmann, P. Folly, A. Sarbach, P. Brodard, R. Baltensperger, J. Therm. Anal. Calorim., 2014, DOI: 10.1007/s10973-014-3903-3
3. M. Dellavedova, C. Pasturenzi, L. Gigante and A. Lunghi, Chem. Eng. Trans., 26 (2012), 585.