

Peculiarities of Calorimetric Data Processing for Kinetics Evaluation in Reaction Hazard Assessment

A. Kossoy, P. Misharev, V. Belochvostov, ChemInform St. Petersburg Ltd. (CISP)

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Preface

This material has been presented at 53 Annual Calorimetric Conference almost 20 years ago. Unfortunately because of certain circumstances it has not been published. We say "unfortunately" as the proceedings of this conference can hardly be found freely whereas the matters discussed were important and could be useful for researchers involved in experiments based on DSC or adiabatic technique. As a matter of fact the main ideas of the report remain topical ones and deserve attention of wider audience. We are planning to publish the updated and more in-depth material in the near future, nevertheless it seemed reasonable to make this paper available right now.

Authors are indebted to Tom Hofelich - some ideas presented here came to life after discussions with him and thanks to his valuable comments and suggestions.

(A. Kossoy, July 2016)

Introduction

Calorimetry, as applied to reaction hazard assessment, provides valuable data for evaluating reaction kinetics, which allows solution of miscellaneous problems of thermal safety by using mathematical modeling. A peculiarity of kinetic study for hazard assessment is that the resultant kinetics is intended mostly for runaway simulation, and the results are sensitive to small variations of the kinetic parameters. The reliability of kinetics, in its turn, depends on the elaboration of the methodology of calorimetric experiment. Therefore, some inaccuracies in methodology, often inessential in general practice, become crucial when reaction hazards are investigated. Although numerous publications are devoted to this subject, many problems are still unsolved or are not given due consideration. In particular, the influence of small errors in interpretation of calorimetric data on the resultant kinetics has not been practically discussed. The aim of this article is to bridge this gap by considering some peculiarities of DSC and adiabatic data.

Concerning DSC data, two topics are discussed – sample overheating and heat inertia of a cell. Both result in rather small distortions of a calorimetric response but, if not taken into account, may lead to unsafe kinetics and incompatibility of data.

Regarding adiabatic data, the problem of uncertainty of initial conditions at the onset temperature is considered.

Peculiarities of Data of non-adiabatic Calorimetry

Dynamic Model of a Calorimetric Experiment

To discuss peculiarities of data of non-adiabatic calorimetry, first consider the dynamic model of a calorimetric system (1-3) (see also Fig. 1 and definitions of symbols in Nomenclature):

$$(cm)_s \frac{dT_s}{dt} = m_s \frac{dQ}{dt} - q; \quad (1)$$

$$q = R_t^{-1}(T_s - T_e); T_e = T_e(t) \text{ or} \quad (2)$$

$$T_s = T_e + qR_t \quad (2a)$$

$$m_s \frac{dQ}{dt} = q + R_t (cm)_s \frac{dq}{dt} = q + \tau \frac{dq}{dt}; \quad (3)$$

where $R_t = (\chi S)^{-1}$; $\tau = (cm)R_t$.

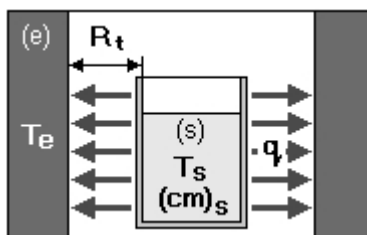


Fig. 1. Simple scheme of the measuring block of a calorimeter.

(e) –environment (furnace). (s) – sample

R_t – thermal resistance; q – heat removal from a sample; $(cm)_s$ – mass heat capacity of the sample and crucible.

This model is well known [1–4]. Here we will discuss two peculiarities.

1. As a rule, sample temperature is not measured directly. At best the sample/reference holder temperature is measured. Heat flux is most frequently the response of a calorimeter. Therefore, using the relationship (2) which bounds heat flux with sample and furnace temperature, the final form of the dynamic model (3) can be derived from heat balance equation (1). (For many DSC devices the reference temperature, T_r , is used instead of T_e .)
2. The intensity of heat exchange in a calorimetric block is always limited. Therefore, part of the heat generated by a reaction is inevitably accumulated in the sample. This results in two important features:
 - a. sample overheating, $\Delta T_s = (T_s - T_e)$, always exists, therefore sample temperature deviates from furnace (or reference) temperature. The magnitude of ΔT_s is proportional to the heat generation in a sample. The overheating and, hence, true sample temperature can be estimated from the calorimeter response (equation (2a)) if the conditions of heat exchange between the sample and thermostat are known. In other words, thermal resistance of a device should be defined because this parameter describes the rate of heat exchange.
 - b. Calorimetric response is always distorted with regard to heat generation rate in a sample. The true heat generation rate, which is the final result of the kinetic experiment, should be reconstructed by applying equation (3), i.e. is subject to deconvolution procedure. From (3), the degree of distortion depends on the time constant of a cell and rate of heat removal. To deconvolute data, the time constant of a device has to be known. Note that thermal resistance and time constant that describe dynamic properties of a device should be determined from specialized calibration experiments (see, for instance, [5]).

In calorimetric kinetic experiments, it is often assumed that deviation of sample temperature as well as distortion of a response is small enough to be neglected. Therefore, reference (or furnace) temperature and original calorimetric response are used for further analysis. The applicability of this assumption needs to be checked carefully especially if the final aim of the study is reaction hazard assessment.

Influence of Sample Overheating on Results of Kinetics Evaluation

All the results presented in this section concern the simple N-order reaction model

$$\frac{d\alpha}{dt} = (1 - \alpha)^n \cdot k_0 \exp\left(-\frac{E}{RT_s}\right); \quad \frac{dQ}{dt} = Q_\infty \cdot \frac{d\alpha}{dt}, \quad (4)$$

but the conclusions are valid for reactions of any kind.

Let us firstly consider what happens if overheating is neglected. For this purpose, a set of simulated heat flux DSC data is used, but the conclusions are valid for any other type of non-adiabatic calorimetry. The exothermic N-order reaction has been modeled in accordance with the equation (1) for linear heating mode. To simulate various overheatings thermal resistance values ranging from 2 to 17 K/W were used. Fig. 2 depicts typical heat generation rate curve and sample temperature.

Fig. 3 demonstrates the influence of overheating on deformation of the dQ/dt curve. Overheating induces thermal acceleration of a reaction.

If the kinetics is evaluated without taking into account deviation of the sample temperature from linearity, every data set can be fitted very well (see an example in Fig. 4), but kinetic parameters deviate from true values proportionally to the overheating. Fig. 5 illustrates the increase of effective activation energy caused by the increase of maximal overheating.

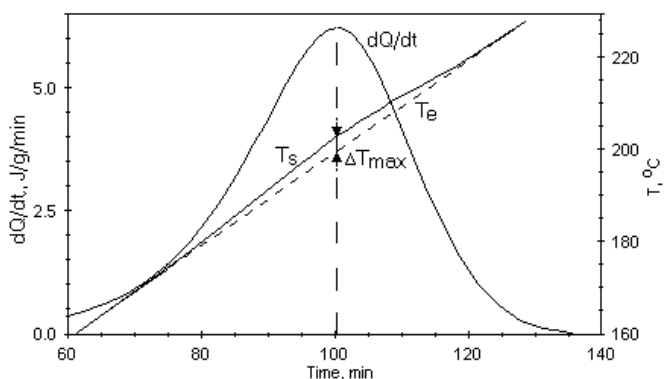


Fig. 2. Deviation of sample temperature, T_s , from linearity due to an exothermic reaction.

Thermal mode – linear heating $T_e = T_0 + \beta t$; $T_0 = 100^\circ\text{C}$, $\beta = 1$ K/min; $(cm)_s = 4$ J/g, $R_t = 10$ K/W. Kinetics: $k_0 = 1.96 \times 10^{11} \text{ s}^{-1}$; $E = 130$ kJ/mol; $n = 1$; $Q_\infty = 200$ J/g.

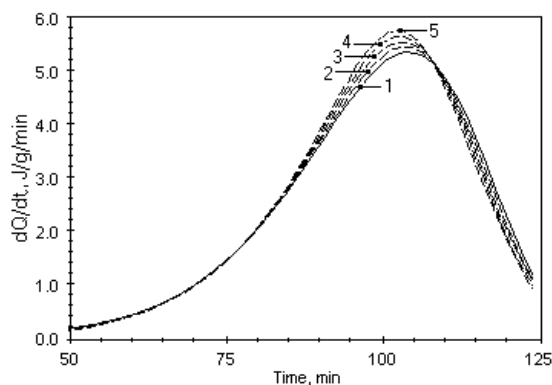


Fig.3. Deformation of a calorimetric response due to sample overheating.

Maximal overheating ΔT_m : 1 - 0°C ; 2 - 0.6°C ; 3 - 1.1°C ; 4 - 1.5°C ; 5 - 2.1°C .

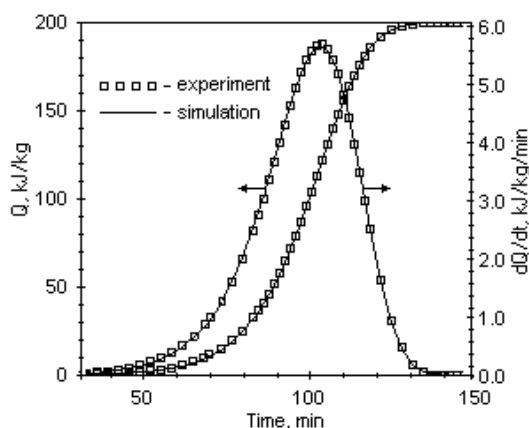


Fig. 4. Example of fitting of pseudo-experimental data provided by the created kinetics (data correspond to the maximal overheating 1.5°C).

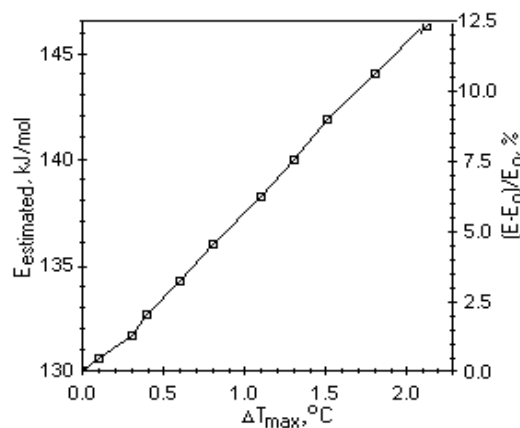


Fig. 5 Dependency of estimates of activation energy on the sample overheating, ΔT_{max} . (E_0 – true value)

The reaction rate increases due to deviation of the sample temperature from the linear ramp. If to neglect sample overheating when evaluating kinetics, higher activation energy than the real one is obtained. Depending on the overheating, the error in estimating activation energy ranges from about 1% to 12%.

What is the permissible level of the errors or, in other words, what is the maximal overheating which can still be neglected? The answer depends strongly on the final aim of the kinetic study. Let us consider two practical cases.

1. The kinetic model is to be used for simulation of reaction behavior under specified conditions, for instance, at constant environmental temperature. Fig. 6 depicts the results of such simulation for three sets of kinetic parameters that correspond to zero, moderate and largest overheating. Evidently, the difference between simulated results is small enough and overheating can be neglected without any essential consequences.
2. The kinetic study is aimed at reaction hazard assessment and kinetics will be used for prediction of reaction behavior under adiabatic conditions. Results of simulation for this case are presented in Fig. 7. Even small overheating, if neglected, noticeably affects the result. If the overheating exceeds 1°C , the prediction of such important parameters as maximal reaction rate and especially time to maximum rate becomes uncertain. The origin of this phenomenon is very high sensitivity of simulation results to a small variation in the kinetic parameters when adiabatic conditions are modeled. At the very least one should estimate overheating before using data for kinetic evaluation and correct the sample temperature if overheating exceeds 0.5°C .

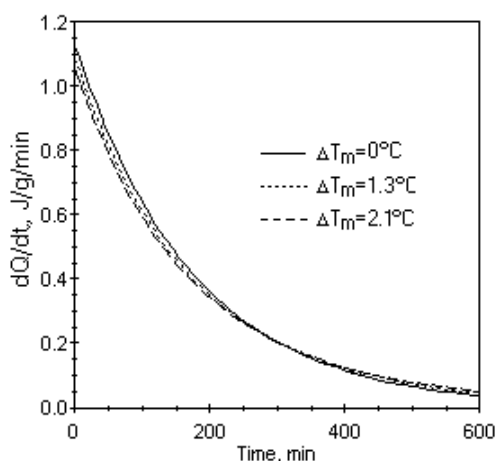


Fig. 6. Simulation of the reaction which proceeds at constant environmental temperature $T_e=170^\circ\text{C}$ in well stirred BATCH. Sample mass – 2g, overall heat transfer $\chi S=0.14$ W/K.

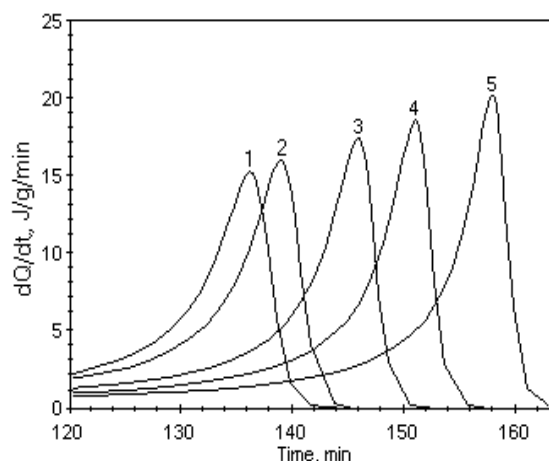


Fig. 7. Simulation of the reaction under adiabatic conditions. $T_0=150^\circ\text{C}$. Kinetics based on data with: 1 - $\Delta T_m=0^\circ\text{C}$; 2 - $\Delta T_m=0.4^\circ\text{C}$; 3 - $\Delta T_m=1.1^\circ\text{C}$; 4 - $\Delta T_m=1.5^\circ\text{C}$; 5 - $\Delta T_m=2.1^\circ\text{C}$

Influence of temperature changes within a sample on the results of kinetics evaluation was analysed in various papers (see, for instance, [6, 7]). Nevertheless it was expedient to discuss this phenomenon again because of its importance for investigation of reaction hazards.

Influence of Data Deconvolution on the Results of Kinetics Evaluation

Lack of deconvolution of calorimetric data represents another source of errors when kinetics is used for hazard assessment. To demonstrate the influence of data deconvolution we will use real data regarding the decomposition of a 20% solution of di-tert-butyl peroxide (DTBP) in toluene obtained by DSC and adiabatic calorimetry (ARC). Here, the ARC data will be considered as a reference.

A flame-sealed glass capillary cell and silver holder [8] were used for DSC experiments. The time constant, $\tau=6$ s, is small and even at high heating rate, maximal overheating is negligible small. Assuming that precise value of the time constant is unknown several approximate values were used for deconvolution. Fig. 8 shows that the difference between the curves deconvoluted at various values of τ is small (the spread at the worst point doesn't exceed 10% of maximal rate).

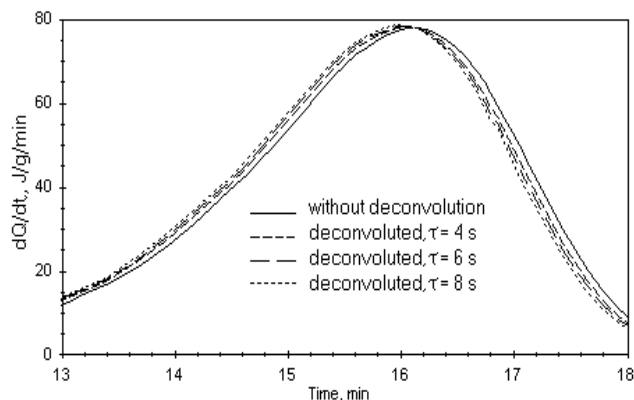


Fig. 8. Influence of the time constant value on the results of deconvolution.

DSC data: Sample – DTBP, sample mass – 0.76 mg, heating rate – 10 K/min, $\Delta T_m < 0.05^\circ\text{C}$.

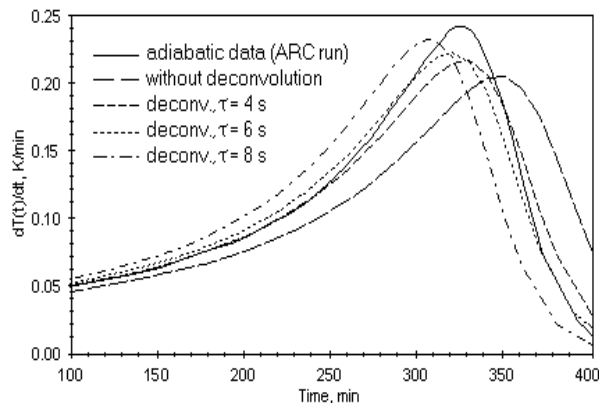


Fig. 9. Comparison of experimental (ARC) data and results of simulation of reaction proceeding under the same adiabatic conditions.

When these data were used for kinetics evaluation of the simple N-order reaction model, in all the cases data fitting was very good and the difference between resultant kinetic parameters is extremely small (Table 1).

Results of kinetics evaluation based on data deconvoluted at various time constants

Parameter	$\tau = 0$ s	$\tau = 4$ s	$\tau = 6$ s	$\tau = 8$ s
$\ln(k_0)$, $\ln(1/\text{sec})$	35.58	35.65	35.72	35.81
E, kJ/mol	153.64	153.67	153.84	154.02
n	1.036	1.037	1.036	1.029
Q_∞ , kJ/kg	193.4	193.4	193.3	193.3

Then every kinetic set was used for simulation of the reaction under the conditions of the ARC run. The results presented in Fig. 9 indicate that, despite very small differences in kinetic parameters, adiabatic curves differ significantly. Only data deconvoluted using the true value of the time constant provide accurate kinetics.

Fig.10 depicts fitting of both adiabatic and DSC data by the kinetics based on properly deconvoluted DSC data (kinetic parameters corresponding to $\tau = 6$ s from Table 1 were used for simulation).

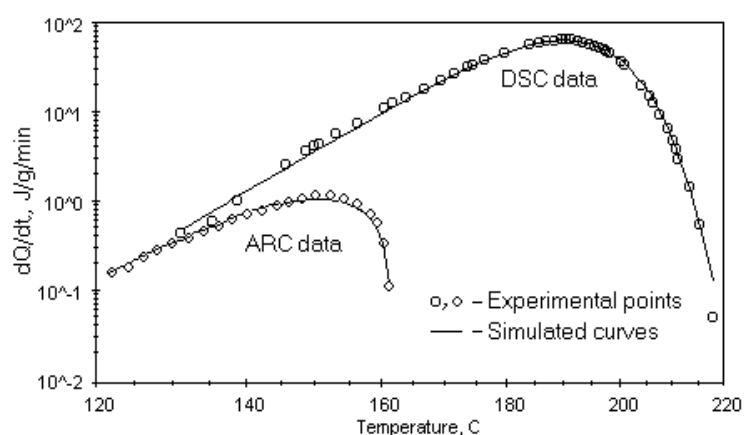


Fig. 10. Compatibility of adiabatic data and kinetics based on properly prepared DSC data.

Data of scanning calorimetry have been considered here. But the problem of proper deconvolution is even more important for results of isoperibolic calorimetry (see [4, 10]).

As in the case of sample overheating, the adiabatic mode is found to be highly sensitive to small variations of kinetic parameters. It is clear that only carefully prepared calorimetric data allow evaluating kinetics which is valid for hazard assessment. It is also evident that the correct procedures of data processing will give proper results only if all the details of an experiment are elaborated.

Features of Adiabatic Data. Uncertainty of Initial Conditions

Formulation of the Problem

An important problem with adiabatic data is the uncertainty of the reactant state at the onset temperature of the adiabatic mode. The problem originates from the simple facts that it is just impossible to maintain adiabatic conditions from the beginning of an experiment and the sensitivity of an adiabatic calorimeter is limited. It is common practice to apply one or another type of thermal initiation. The adiabatic mode is established when a calorimeter first detects heat generation by the reaction. Usually it is assumed that due to high sensitivity of the calorimeter the conversion at the detected onset temperature is negligible ("zero" assumption) although it is evident that reaction started before the onset and conversion is non-zero but there is no way to determine it directly. Nevertheless, it turns out that even very small but nonzero conversion strongly affects the reaction course and kinetics evaluated under "zero" assumption may be unsafe or even completely wrong [9]. In this work, a more detailed consideration of the problem is given and a simplified solution is proposed.

Firstly consider a simple example of single stage reactions of two types:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha); \quad \text{where } f(\alpha) = \begin{cases} (1-\alpha)^n & \text{case 1 - N - order reaction} \\ (1-\alpha)(\alpha+z) & \text{case 2 - auto catalytic reaction} \end{cases}$$

Let's suppose that at the detected onset temperature the real conversion degree is 1%, i.e. initial conversion $\alpha_0 = 0.01$, and the typical value of autocatalysis constant is $z = 0.01$. Then we will obtain:

- case 1: $f(\alpha_0) = 0.99$, initial reaction rate = $0.99k$;
- case 2: $f(\alpha_0) \approx 0.02$, initial reaction rate = $0.02k$.

At the same time with "zero assumption" $\alpha_0 = 0$ we will have:

- case 1: $f(\alpha_0) = 1$, initial reaction rate = k ;
- case 2: $f(\alpha_0) = 0.01$, initial reaction rate = $0.01k$.

Obviously, if we use the zero assumption, we will get a quite small error in the estimate of the rate constant, k , for non-accelerating reaction and two times overestimate of k for the auto catalytic reaction. It may seem that the uncertainty problem is important only for self-accelerating reactions, but, as it will be shown, even for non-accelerating reactions the uncertainty in initial conditions may lead to serious errors.

The general way of avoiding the problem is to take into account all the thermal history of a sample instead of only the adiabatic part. From the mathematical point of view it means that one should apply the complete model of a reactor:

$$\begin{aligned} \text{Kinetic Equation: } & \frac{d\alpha}{dt} = f(\alpha) \cdot k_0 \exp\left(-\frac{E}{RT_s}\right); \quad \frac{dQ}{dt} = Q_\infty \cdot \frac{d\alpha}{dt} \\ \text{Heat Balance Equation: } & c_s m_s \varphi \frac{dT_s}{dt} = m_s \frac{dQ}{dt} - \chi S (T_s - T_e) \end{aligned} \quad (5)$$

with the following boundary and initial conditions:

$$0 < t < t_0; \quad T_e = T_e(t); \quad \chi S > 0$$

$$t_0 < t; \quad T_e = T_s; \quad \chi S = 0$$

$$t = 0; \quad \alpha(0) = 0; \quad T_s = T_{s0}$$

Here χS – overall heat transfer coefficient, t_0 – onset time when the adiabatic mode starts, T_e – temperature of the guard heater (environmental temperature). Depending on the type of a device $T_e(t)$ is linear temperature ramp (VSP) or stepwise heating which corresponds to the heat – wait – search procedure (VSP, ARC). Fig. 11 illustrates the method of data interpretation described by the model (5).

To apply this model, parameters of heat transfer should be known. Unfortunately, their determination is not provided by any commercial instrument (this is subject of calibration procedure, which is typically not supported). Nevertheless even in these circumstances the approximate method can be proposed for solving the problem of initial conditions.

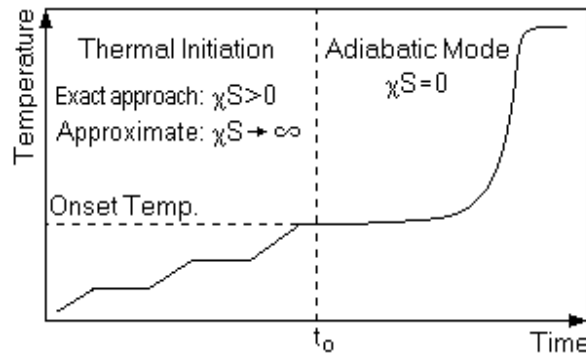


Fig. 11. Interpretation of data of an adiabatic experiment.

Method of Solving the Problem

The approximate method is based on the fact that, because of the relatively high sensitivity of adiabatic calorimeters, the heat generated during the reaction's initiation is very small. Therefore, we can neglect heat accumulation in a sample and reckon that at $0 < t < t_0$; $\chi S \rightarrow \infty$, i.e. heat is not accumulated in a sample at all. In this case the model (5) is reduced to the following form (see also Fig 11):

Mode		Boundary conditions:	Heat Balance:
Thermal initiation $0 < t < t_0$	exact model	$\chi S > 0$ (limited)	$c_s m_s \varphi \frac{dT_s}{dt} = m_s \frac{dQ}{dt} - \chi S (T_s - T_e)$
	approximate	$\chi S \rightarrow \infty$	$T_s = T_e$
Adiabatic $t > t_0$		$\chi S = 0$	$c_s \varphi \frac{dT_s}{dt} = \frac{dQ}{dt}$

There still exists some uncertainty regarding heat generation because we don't know the amount of heat removed during initiation. However temperature response, which is measured directly, is valid and can be used for parameters estimation.

To apply the method described, experimental data of an adiabatic calorimeter should be prepared in an special way:

- during the thermal initiation, $0 < t < t_0$, overall heat transfer is infinite (in practice it is enough to set $\chi S \approx 5 - 10$ W/K), and sample temperature is considered to be equal to oven temperature;
- after the detected onset temperature, $t > t_0$, no heat removal takes place and sample temperature is used as usual adiabatic response (Fig. 11).

Consider now an example of application of this approach on the basis of real ARC data ($m_s = 3.6$ g; $\varphi = 2.174$) related to the two-stage consecutive non-autocatalytic reaction $A \rightarrow B \rightarrow C$:

$$\begin{aligned} \frac{d\alpha}{dt} &= k_{01} \exp\left(-\frac{E_1}{RT}\right) \cdot (1-\alpha)^{n_1} \\ \frac{d\gamma}{dt} &= k_{02} \exp\left(-\frac{E_2}{RT}\right) \cdot (\alpha-\gamma)^{n_2} \\ \frac{dQ}{dt} &= Q_{\infty 1} \frac{d\alpha}{dt} + Q_{\infty 2} \frac{d\gamma}{dt}; \end{aligned} \quad (6)$$

where α and γ - conversions of reactant, A, and product, C, correspondingly.

This complex kinetics has been evaluated by using the same non-linear optimization method as was used in previous section. The whole temperature response (including thermal prehistory) was used for parameters' estimation. Fig. 12 shows the quality of data fitting.

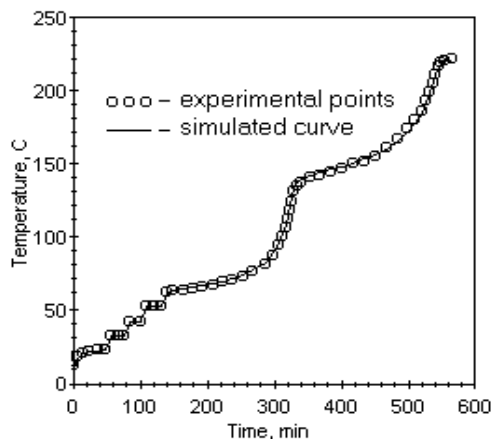


Fig. 12. Results of kinetics evaluation based on complete temperature response (true kinetics).

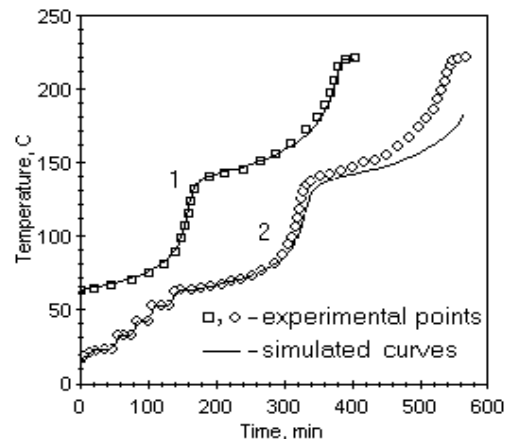


Fig. 13. Results of kinetics evaluation based on adiabatic fragment of data (unsafe kinetics).

- 1 – fitting of the adiabatic fragment of experimental data;
- 2 – discrepancy between experimental and simulated results when thermal prehistory is taken into account.

If we evaluate kinetics using, as usual, the adiabatic fragment of data and “zero assumption” we can also obtain a good data fit (Fig. 13, curve 1). But if we then use this kinetics for simulation of the whole thermal history of a reactant the result of simulation will be wrong (Fig. 13, curve 2). The reaction kinetics obtained by using approximate method is more reliable as it absorbs almost all the available information about the process.

Attention should be drawn to the following important facts.

1. Whereas the difference between simulated and experimental data for the first stage is not very big it induces much larger difference for the second stage.
2. In some cases, the influence of uncertainty of initial conditions may be very strong even for non-accelerating reactions. At the same time the difference in kinetic parameters is small (Table 2) and, again, the specific feature of adiabatic mode is revealed – extremely high sensitivity of the model to small variation of the parameters' values.

Table 2

Comparison of results of kinetics evaluation based on traditional and advanced methods.

Parameter	1 stage		2 stage	
	Approximate method	"zero assumption"	Approximate method	"zero assumption"
$\ln(k_0), \ln(s^{-1})$	31.76	31.73	18.15	18.06
E, kJ/mol	120.08	120.077	99.76	99.75
n	1.94	2.02	0.71	0.61
Q_∞ , kJ/kg	334.4	330.9	357.2	349.6

With reliable kinetics in hand there is now the possibility to estimate the conversion degree at the detected onset temperature. It turns out that $\alpha_0=1.3\%$, at that the second stage is much slower than the first one so that $\gamma_0 \approx 0$.

Conclusions

Application of the elaborate methodology of calorimetric experiments is especially important when reaction hazards are investigated. Only in this case do experimental data allow evaluation of reliable kinetics applicable for runaway modeling. In many cases, mathematical simulation based on kinetics is the only possibility to compare experimental results obtained by different types of calorimeters or under different conditions. Therefore, minor drawbacks of experiments that produce inaccurate kinetics can cause the seeming incompatibility of data of various techniques. Procedures of data processing and kinetics evaluation that were discussed or mentioned in this paper (specifically, non-linear optimization) require application of state-of-the-art mathematical and numerical methods [10]. Therefore they are rather labor-consuming and can hardly be applied in practice if not supported by the appropriate tools. The commercial software developed by ChemInform Ltd. [11] is the very tool. Specifically the TDPPro, ADPro and ForK applications were used for implementing this work.

Note that ADPro and ForK have the special options that implement the advanced method of adiabatic data interpretation.

Nomenclature

c – specific heat;	T – temperature;
m – mass;	Q – specific heat generation due to a reaction
t – time;	Q_∞ – specific heat effect of a reaction/stage;
R_t – thermal resistance of a calorimetric cell;	n – reaction's order;
$R_t = (\chi S)^{-1}$	E – activation energy;
τ – time constant of a calorimetric cell;	R – universal gas constant;
q – heat removal from a sample;	α, γ – conversions of reactants/products
χ – heat transfer coefficient;	k – rate constant of a reaction/stage
S – surface of heat exchange;	k_0 – pre exponential factor;
φ – heat inertia of a calorimetric cell:	z – auto catalytic constant
$\varphi = 1 + (cm)_b / (cm)_s$	

Indexes:

s – sample;	e – environment (thermostat);
b – bomb;	o – initial value of a variable/parameter

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