

# Identification of Kinetic Models for the Assessment of Reaction Hazards

A. Kossoy, Yu. Akhmetshin

ChemInform St. Petersburg (CISP) Ltd. St. Petersburg, Russia; Kossoy@cisp.spb.ru (for correspondence)

Process Safety Progress (Vol.26, No3), Published on behalf of the AIChE, September 2007, pp. 209-221

*The assessment, control and mitigation of reaction hazards is primarily based on the use of kinetic models. These kinetic models are used for the assessment of reaction hazards, the operation and control of the reactor, the design of emergency relief systems, and estimation of the consequences of a reaction runaway, to name a few. The validity of these assessments depends highly on the validity of the kinetic model employed.*

*Several steps are required to identify a suitable kinetic model. This includes:*

- *Selection of the model type.*
- *Estimation of the model's parameters using available data.*
- *Validation of the model.*

*This paper discusses each of these steps in detail and identifies problems associated with each step. Several practical examples are used to demonstrate these problems.*

*The results show that: 1) the results are sensitive to a number of assumptions, 2) mistakes may originate from misinterpretation of the thermal data, and 3) computational methods do exist to provide suitable kinetic models for hazard assessment.*

*The analysis employed assumes a batch reaction system, since most of the kinetic data available is derived from batch calorimetric equipment.*

*Keywords: kinetics evaluation, parameters estimation, simulation, hazard assessment*

## INTRODUCTION

One of the most important stages in the investigation of chemical reactions is the identification of a reaction kinetic model. These models may then be used for many important purposes, such as optimization of the chemical process, assessment of the reaction hazards, design of emergency relief systems (ERS), and so forth. The validity of these studies strongly depends on the reliability of the kinetic model which is defined by the proper choice of a mathematical model of the reaction

and the validity of the methods used for the kinetics evaluation. Therefore, it is not surprising that many books and articles are devoted to various aspects of kinetic analysis [1-9]. A majority of these publications are related to data treatment in thermal analysis [1-6] or in chemical engineering [7-9]. A very limited number of articles are available that consider specific problems of kinetics evaluation for hazard assessment [10-15].

Comparative analysis of these publications shows that the most in-depth approach to kinetics evaluation is used in chemical engineering. Quite comprehensive methods are applied in thermal analysis, although less attention is paid to the thermal mode of the sample. In general, kinetics evaluation methodology for reaction hazards investigation is still characterized by the use of the simplest models and simplest methods for their creation (see for instance [14]). This occurs in spite of the fact that the results of a reaction runaway simulation are extremely sensitive to small errors in the kinetics. This situation is improving as more and more publications appear discussing and demonstrating the advantages of the up-to-date technique of kinetics analysis [15, 16]. Nevertheless such advanced methods are still not common practice.

This state of affairs suggests that the consideration of problems relating to kinetics evaluation for hazard assessment with the focus on the specific features of the data used and the final tasks to be solved remains a question of vital importance. Many aspects of kinetic evaluation have already been analyzed in detail and therefore there is no need to develop any new methods. What is really required is to carefully select the most appropriate and well grounded ones and make the necessary adjustments. This paper attempts to achieve this.

The general procedure intended for creation of a kinetic model includes four typical steps:

- obtaining and preparing experimental data;
- choosing an appropriate kinetic model;
- estimating parameters for the model that provide the best data fit;
- selecting the most adequate model if several different models have been proposed.

The resulting model can then be applied to the problem at hand. To a large extent the kinetics evaluation for hazard assessment is coupled to the features of the final aim of the investigation. Simplified models that describe some overall characteristics of a reaction, like heat or gas generation, can be successfully applied for analysis of thermal stability, determination of critical condition of thermal explosion, etc. On the contrary, more detailed models capable of describing the time change in the mixture composition should be used for designing inherently safer processes, runaway simulation in a reactor, or sizing relief vents because the time variation of the mixture composition and the corresponding change of mixture properties may strongly affect the process mode and therefore must be taken into account.

#### CHOICE OF A KINETIC MODEL

A chemist deals with wide variety of reactions that differ significantly from each other: homogeneous, heterogeneous catalytic, polymerization, biochemical; topochemical solid state reactions, etc. Different types of kinetic models should be used to take into account specific features of chemical reactions of different classes.

Reaction hazards investigation deals usually with homogeneous or pseudo homogeneous reactions. Furthermore, due to the lack of information about the process (especially about secondary reactions) one has to apply a simplified kinetic model that does not describe the detailed mechanism, but can describe properly the main characteristics of a reaction. Two types of kinetic models are very pertinent in this case – formal and descriptive ones. The choice between them depends on the knowledge about a reaction and on the final problem we are going to solve.

#### Types of kinetic models: descriptive and formal models

##### *Descriptive Models*

Descriptive models are formulated in terms of concentrations and, therefore, can describe the reaction's mechanism in more detail. The applicability of these models can be expanded by accepting the generalized law of mass action (GLMA), i.e. the rate is proportional to the product of the concentrations raised to an order.

GLMA includes the particular case of the exact law of mass action (LMA) when the orders coincide with the stoichiometric coefficients. For the multi stage reaction which is defined by the stoichiometric scheme

$$\sum_{i=1}^N (\beta_{ji} - \nu_{ji}) A_{ji} = 0 \quad ; j = 1, \dots, M \quad (1)$$

the rate of the j-th step is given by the equation

$$r_j = k_j \prod_{(i)} [A_{ji}]^{\nu_{ji}} \quad \text{for LMA and} \quad (2a)$$

$$r_j = k_j \prod_{(i)} [A_{ji}]^{n_{ji}} \quad \text{for GLMA; } j = 1, \dots, M, \quad (2a)$$

and the rate of variation of the i-th species concentration is given by

$$\frac{d[A_i]}{dt} = \sum_{(j)} (\beta_{ji} - \nu_{ji}) r_j \quad (2b)$$

Here  $\nu_{ji}$ ,  $\beta_{ji}$  are the stoichiometric coefficients of reactants and products of the j-th stage;  $n_{ji}$  are the reaction orders,  $[A_{ji}]$  denote the concentrations of species;  $k_j(T) = k_{j0} \exp(-E_j/RT)$  is the rate constant of a step.

The model is supplemented with the corresponding initial conditions and the response equations, that is, the equations that bound stage rates with the observable responses (heat or gas production, species concentrations, etc.):

$$\frac{dQ}{dt} = \sum_{(j)} Q_j^\infty r_j; \quad \frac{dG}{dt} = \sum_{(j)} G_j^\infty r_j; \quad [A_{ji}] \quad (3)$$

Descriptive models can be applied to the reactions proceeding in a BATCH, semi-BATCH or continuous stirred reactor functioning in various thermal modes.

In order to use these quite powerful models, some requirements should be satisfied:

- An initial idea regarding the chemistry of a reaction should be formulated;
- Experimental data on the calorimetric and concentration response must be collected.
- Basic properties ( $C_p(T)$ , density, molecular mass) of the species should be known.

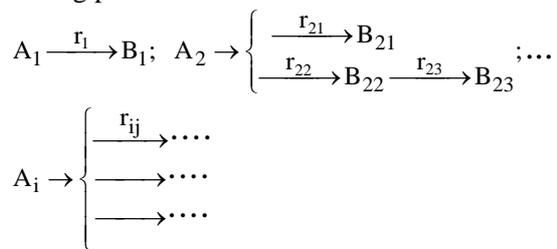
The descriptive models can be used for the analysis of the thermal stability of a chemical product and the determination of reactive hazard indicators (e.g. NFPA reactivity rating, adiabatic time to maximum rate [16]). However, the advantages are maximized when these models are applied to the simulation of

runaway in a reactor equipped with ERS, design of inherently safer chemical process and its optimization, and so on.

### Formal models

Formal models are based on the assumption that the conversion degrees are the state variables of a reacting system. Typically, we need to use such an approach when there is inadequate information for constructing a more detailed reaction mechanism, and only some overall responses (such as heat and gas generation) are available from experiment, but not the composition variation. Specifically such a situation occurs when investigating reactions in solids, secondary reactions that are triggered at elevated temperatures under accidental conditions, etc.

Formal models can represent complex multi-stage reactions that may include several independent, parallel and consecutive stages. It is demonstrated by the following pattern:



A formal model is presented by the system of ordinary differential equations

$$\frac{d\alpha_i}{dt} = \sum_{(j)} r_{ij}; r_{ij} = k_{ij}(T) \cdot f_j(\alpha_i); k_{ij}(T) = k_{ij0} \exp\left(-\frac{E_{ij}}{RT}\right)$$

supplemented with the appropriate initial conditions and the responses equations:

$$\frac{dQ}{dt} = \sum_{(i)} \sum_{(j)} Q_{ij}^{\infty} r_{ij}; \frac{dG}{dt} = \sum_{(i)} \sum_{(j)} G_{ij}^{\infty} r_{ij}; \dots \quad (5)$$

Let us cite some examples of formal models.

#### 1. Simple single-stage reaction $A \rightarrow B$ :

$$\frac{d\alpha}{dt} = k_0 e^{-\frac{E}{RT}} f(\alpha); f(\alpha) = \begin{cases} (1-\alpha)^n & \text{- N - order model} \\ (1-\alpha)^{n1} (\alpha^{n2} + z) & \text{- model of generalized autocatalysis} \\ (1-\alpha)(-\ln(1-\alpha))^n & \text{- Avrami - Erofeev model} \end{cases} \quad (6a)$$

#### 2. Reaction which includes two consecutive stages: $A \rightarrow B \rightarrow C$ :

$$\frac{d\alpha}{dt} = k_{01} e^{-\frac{E_1}{RT}} (1-\alpha)^{n1}; \frac{d\gamma}{dt} = k_{02} e^{-\frac{E_2}{RT}} (\alpha-\gamma)^{n2} \quad (6b)$$

where  $\alpha$  and  $\gamma$  are the conversions of the reactant A and product C respectively.

3. Two parallel reactions  $A \rightarrow B + \dots$  - initiation stage;  $A + B \rightarrow 2B + \dots$  - autocatalytic stage, that represent very useful model of full autocatalysis:

$$\frac{d\alpha}{dt} = r_1(\alpha) + r_2(\alpha); r_1(\alpha) = k_1(T)(1-\alpha)^{n1}; r_2(\alpha) = k_2(T)\alpha^{n2}(1-\alpha)^{n3} \quad (6c)$$

For simple, single stage reactions it is possible to establish a one-to-one correspondence between concentrational and formal model by using the algebraic transformation, thus allowing easy analytical data treatment. Historically, it was how formal models appeared. In the general case of more complex, multi-stage models, the transformation becomes impossible [8]; therefore complex formal models should be considered as a special class of kinetic models that don't have any relations with concentrational ones. Today, numerical methods allow for the easy handling of complex concentrational models and there is no urgent need to transform them to simpler forms. It is much safer and productive to completely separate two classes of models even in simplest cases.

The nature of the formal models imposes restrictions on their applicability:

- These models cannot take into account changes of composition of the reacting mixture<sup>(4)</sup> due to non-kinetic reasons, such as feed of a reactant, removal of volatile components of a mixture, etc.
- The created kinetics is valid only for the mixture composition investigated [6],
- The models are only valid for analysis of BATCH reactors functioning in various thermal modes. They cannot be applied for simulation of semi-BATCH or continuous reactors;
- They don't allow reliable simulation of changes of physical properties of a mixture due to variation of its composition.

Nevertheless, the formal models are very flexible and convenient to use. For instance, they are almost exclusively applied in the thermal analysis area. In reaction hazard assessment formal models can be successfully used for:

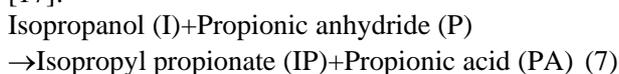
- Analysis of thermal stability of a product and determination of reactive hazard indicators.
- Simulation of a runaway in a BATCH reactor.

- Simulation of thermal explosion in solids for hazard assessment related to their storage and transport.

Moreover, with some precautions, formal models can also be used for simulation of thermal explosion in liquids or for runaway simulation in conjunction with vent sizing, when the mixture properties don't depend strongly on its composition or when it concerns gassy systems, etc.

#### Choice of the appropriate type of a model

The following example illustrates how to choose between two types of models. Consider the esterification reaction, which was proposed for ERS round-robin test [17]:

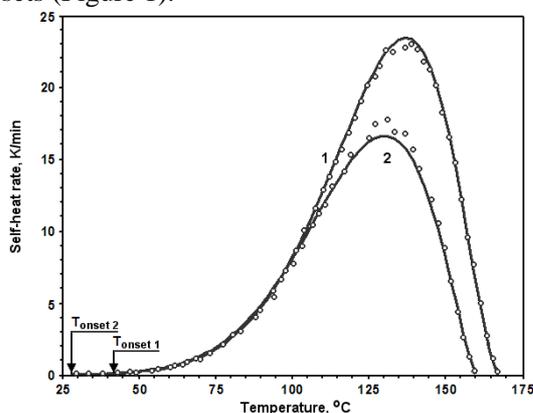


The kinetics is intended for simulation of the runaway in a BATCH equipped with the ERS. Two adiabatic data sets for different onset temperatures 25 °C and 35 °C have been used for kinetics evaluation. Thermal inertia for both these runs was the same:  $\varphi=1.09$ .

At first the formal model of full autocatalysis (6a) coupled with the heat balance equation

$$c_s \varphi \frac{dT_s}{dt} = Q^\infty \frac{d\alpha}{dt} \quad (8)$$

had been created assuming that the sample heat capacity is constant. It ensured satisfactory fitting of both data sets (Figure 1).

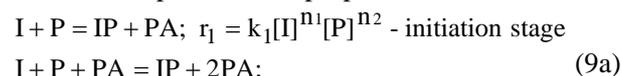


**Figure 1.** Fitting data for the esterification reaction. (1)– onset temperature 35 °C; (2) - onset temperature 25 °C; ○○○○ - experimental points, — - simulation

Nevertheless applying this model to runaway modeling and ERS design will give incorrect and unsafe results. The reason is that the properties of the reacting mixture depend on its composition, which changes along the reaction course. For instance, the overall vapor pressure of volatile components,  $P_v$ , at the initial composition is 2.1 bar at 120 °C; whereas, for the final

composition at the same temperature  $P_v = 0.9$  bar. Therefore, sizing the vent will be incorrect if the variation of  $P_v$  is not taken into account. The heat balance would be also incorrect because the mixture heat capacity significantly depends on its composition (the final value is 1.3 times higher than the initial one).

The following descriptive autocatalytic model provides a proper description of the effects due to mixture composition and properties:



$r_2 = k_2[I]^{n_3}[P]^{n_4}[PA]^{n_5}$  - self - accelerating stage  
 $\frac{d[I]}{dt} = \frac{d[P]}{dt} = -r_1 - r_2$ ;  $\frac{d[IP]}{dt} = \frac{d[PA]}{dt} = r_1 + r_2$ ;  
 $\frac{dQ}{dt} = Q_1^\infty r_1 + Q_2^\infty r_2$  (9b)

Here [I], [P], [IP] and [PA] denote concentrations of isopropanol, propionic anhydride, isopropyl propionate and propionic acid, respectively. It is assumed (see the stoichiometric scheme (9a)) that the self-acceleration is caused by generation of the acid. The model provides a slightly better data fit because more accurate physical properties are used.

The crucial role of physical properties in process simulation is well recognized [18, 19]. The less understood fact is that properties used for kinetics evaluation may also strongly affect the kinetic parameters. The most robust results of the whole study will be guaranteed if the same properties are used both for kinetics evaluation and for simulation. The following example demonstrates what may happen if this rule is not followed.

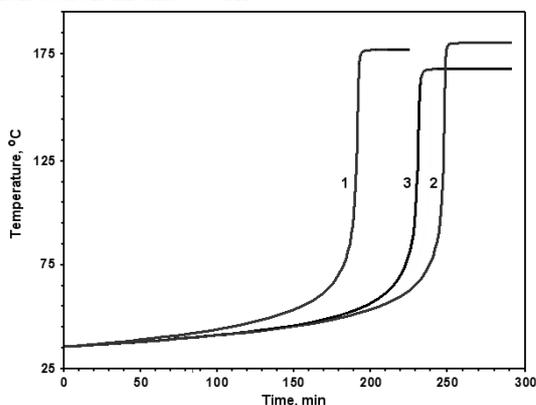
Kinetic parameters of the model (9a) – (9b) have been estimated by using composition and temperature dependent mixture properties (variable properties). The properties of the mixture at current composition were calculated from the temperature-dependent properties of species.

The reaction course under pure adiabatic conditions ( $\varphi=1$ ) was then simulated for 3 cases:

- using the same variable properties of the mixture (Figure 2, curve 1);
- using the composition-dependent properties, that is, properties of the reacting mixture of the current composition were calculated from constant species properties (curve 2);
- using constant properties of the mixture (curve 3).

It is clearly seen from Figure 2 that the physical properties have a dramatic effect on the reaction course. The use of approximate properties may result in unsafe estimates. In our case, the adiabatic time to maximum rate differed by as much as 20 to 30%.

Correct calculation of mixture properties is possible when a descriptive concentration-based kinetic model is applied. A formal model cannot predict the change of mixture composition. In such cases one needs to use overall properties, in particular the heat capacity. Typically the properties are assumed to be constant. The question arises: which values should be used in this case. It was shown in [19] that for runaway simulation “the most accurate value of the heat capacity to use is half the value of the heat capacity at the start and at the end of the reaction”. Hence, the same value must also be used for kinetics evaluation. We followed this recommendation in this work.



**Figure 2** Effect of mixture properties on the prediction of adiabatic reaction course: (1) – composition and temperature dependent properties; (2) – constant properties of the species; (3) – constant properties of a mixture.

### Selection of a model

Model selection arises when several competing models can be proposed and none of them are preferred a priori. This is one of general problems in reaction kinetics studies and is very typical for reaction hazard assessment because the chemistry of a reaction is often unclear (especially if it involves secondary reactions). In such a situation it is very important to get as much data as possible under different conditions. Methods used for generating such complementary data depend on the type of experimental technique applied.

In thermal analysis, experiments are carried out at several different heating rates or by using more complex combined heating modes [3, 5, 6].

In reaction calorimetry, it is a common practice to vary the initial composition of a reacting mixture [6]

and the thermal mode (different initial temperatures, constant and programmed jacket temperature).

In adiabatic calorimetry, it is recommended to change the initial temperature [19] or vary the initial composition of a mixture [15]. Another useful method is to vary the thermal inertia either by using different types of calorimetric cells (bombs), by varying sample masses, or by using different calorimeters (e.g. Phi-Tec or VSP for low- $\phi$  experiments and the ARC for experiments with higher  $\phi$ ). The combination of adiabatic and non-adiabatic (e.g. DSC) methods provides very useful data for model selection [15].

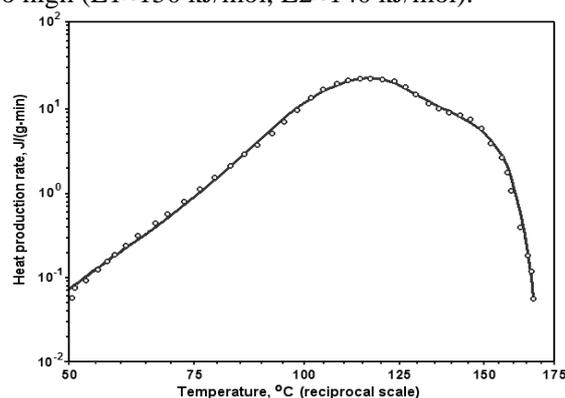
Nevertheless, it is still a common practice in reaction hazard investigations to rely on the results of a single adiabatic experiment. Therefore we will discuss the methods of model discrimination on the basis of data from adiabatic calorimetry. Two examples will be considered.

Example 1. Selection of a formal model.

Polymerization of a monomer has been studied by using the ARC. Only one experiment ( $\phi=1.65$ ,  $T_{\text{onset}}=50^{\circ}\text{C}$ ) was available. The self-heating rate curve (Figure. 3) reveals the complexity of the reaction. The most likely model is the model of two consecutive stages. At first the formal model of two stages of the N-order type

$$\frac{d\alpha}{dt} = k_{01}e^{-\frac{E_1}{RT}}(1-\alpha)^{n1}; \quad \frac{d\gamma}{dt} = k_{02}e^{-\frac{E_2}{RT}}(\alpha-\gamma)^{n2} \quad (10a)$$

had been evaluated. It provided a very good data fit (Figure 3). The only suspicious result was that estimates of both the activation energies seemed to be too high ( $E_1 \approx 150$  kJ/mol,  $E_2 \approx 140$  kJ/mol).



**Figure 3** Adiabatic data on the monomer polymerization;  $\circ\circ\circ\circ$  - experimental points, — - simulation

The temperature range of this reaction is 50-150  $^{\circ}\text{C}$  whereas  $E > 120$  kJ/mol is more typical for reactions that proceed at temperatures higher than 100  $^{\circ}\text{C}$ .

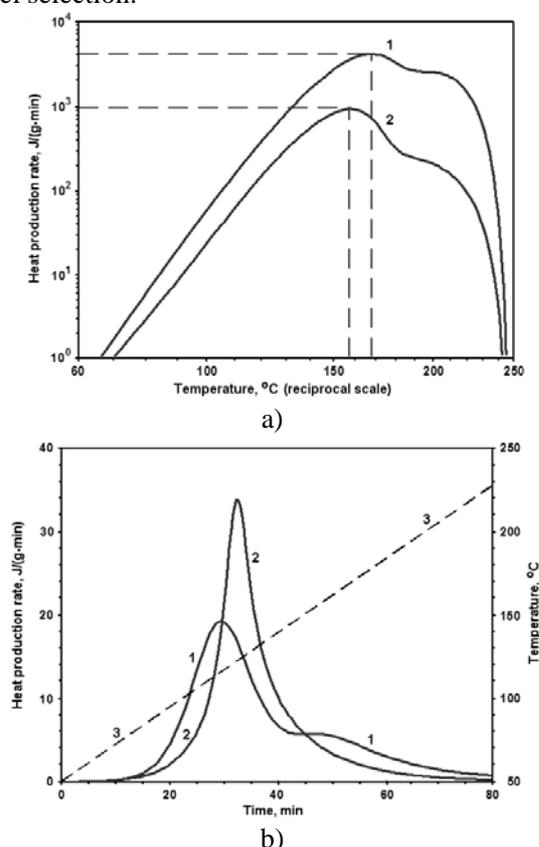
Such a high value for  $E$  may mean that the real reaction is autocatalytic and higher  $E$  compensates for the inability of a chosen (non self-accelerating) model to describe chemical acceleration.

Therefore the alternative model of two consecutive stages with the first autocatalytic stage (10b)

$$\frac{d\alpha}{dt} = k_{01} e^{-\frac{E_1}{RT}} (1-\alpha)^{n1} (z + \alpha^{n2});$$

$$\frac{d\gamma}{dt} = k_{02} e^{-\frac{E_2}{RT}} (\alpha - \gamma)^{n3}$$
(10b)

has been proposed. This model provides practically the same quality of data fitting but the activation energies are noticeably lower:  $E_1 \approx 110$  kJ/mol,  $E_2 \approx 74$  kJ/mol. Additional experiments are required to allow model selection.



**Figure 4** Simulation of the discriminating experiments: (a) adiabatic experiment with  $\phi=1.1$ ; (b) DSC experiment; (1) simulation based on the model (10a); (2) - simulation based on the model (10b); (3) - temperature ramp

Consider at first the possibility of using adiabatic calorimetry for this purpose. In the case of the individual substance one cannot change its initial composition. The onset temperature cannot be changed directly - it is defined by the sensitivity of the calorimeter. The only

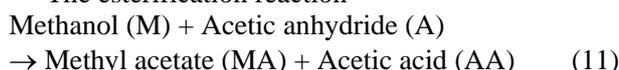
possibility is to change  $\phi$  by increasing the sample mass. The adiabatic experiment at  $\phi=1.1$  has been simulated by using both the competing models (10a) and (10b) coupled with the heat balance equation (8).

The results (Figure 4a) demonstrate a significant difference in prediction provided by two models. The model (10a) suggests about 4.5 times higher maximum adiabatic self heat rate and  $10^\circ\text{C}$  difference in temperatures at which the maximum rates are reached. It is evident that real experiments carried out under the proper conditions will allow easy selection of the model.

Let us now suppose that we can study the sample in scanning mode by using the DSC. To reveal the discriminating ability of the DSC experiment, we simulated it by using both the models at a heating rate of  $2\text{ K/min}$  starting at  $50^\circ\text{C}$  (Figure 4b). As in the previous case the two models give distinctively different predictions and the DSC can be successfully used for model selection.

Example 2. Selection of a descriptive model.

The esterification reaction

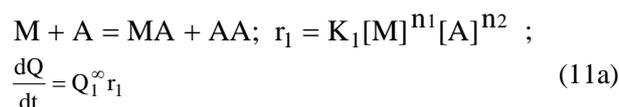


has been studied by using the Phi-Tec adiabatic calorimeter. Two data sets for different initial mixture compositions (mole ratios  $M/A=2$  and  $M/A=6$ ) were available. In both these cases methanol was in excess and the unconsumed part of it acted as a thermal diluent, therefore two data sets demonstrate significant difference in adiabatic temperature rise (Figure 5).

This time descriptive models should be used for kinetics evaluation because they are capable of accounting for the change in initial composition.

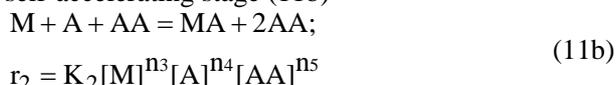
At first the kinetics was evaluated on the basis of the data set A (sample data) with  $M/A=2$  whereas the data set B with  $M/A=6$  (reference data) was used for kinetics validation.

Esterification reactions of this kind are known to be autocatalytic [15, 19, 20] though autocatalysis is quite weak. Therefore the simple single stage  $N$ -order reaction model



is often used for data fitting [21]. As can be seen in Figure 5a (curve 1, solid line) this model, after estimation of its parameters, fits the sample data very well, but it poorly predicts the reaction course for the conditions of the reference data (Figure 5a, compare curves 2 and 3).

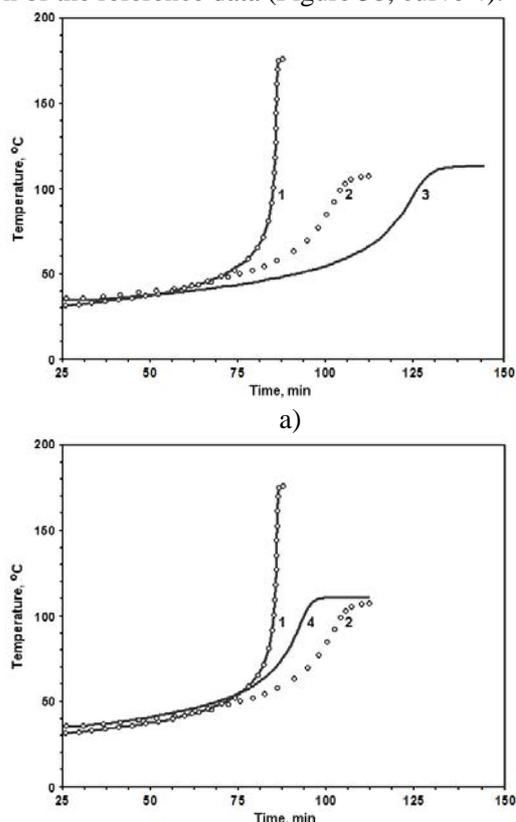
A more complex two-stage autocatalytic model was then used consisting of the initiation stage (11a) and the self-accelerating stage (11b)



coupled with the complete response equation.

$$\frac{dQ}{dt} = Q_1^\infty r_1 + Q_2^\infty r_2 \quad (11c)$$

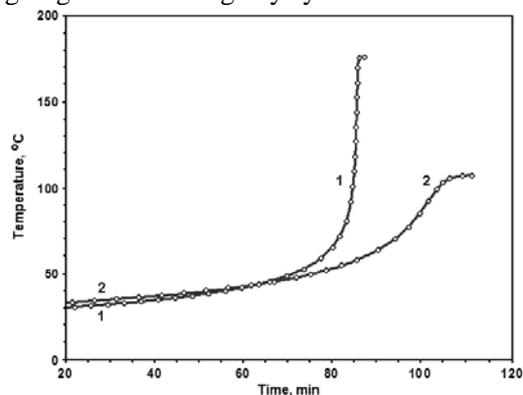
It gives almost the same fit with the sample data (Figure 5b, curve 1, solid line) and ensures better prediction of the reference data (Figure 5b, curve 4).



**Figure 5.** Comparison of two models evaluated from the adiabatic data set A.  $\circ\circ\circ\circ$  - experimental points, — - simulation; (a) –using the N-order model (11a); (b) – using the autocatalytic model (11a)-(11b); (1) - experiment A,  $M/A=2$ ; (2) – reference experiment B,  $M/A=6$ ; (3) – prediction of reference experiment by the model (11a); (4) - prediction of reference experiment by the model (11a) -(11b)

If both the data sets A and B are used for evaluation of the autocatalytic model, the data fit is very good (Figure 6). The single-stage model cannot provide a comparable fit with the experimental data even if both the data sets were used for its evaluation. The autocatalytic model should be selected as the better model. To

conclude this section we want to draw special attention to one important topic. The selection of a more adequate model is of general value for the following simulation but distinction between the autocatalytic model and the non-self accelerating one is particularly important. The peculiarities of an autocatalytic reaction may have such a strong impact on the results that the use of specific approaches is required. For instance, a special theory of thermal explosion for autocatalytic reactions had to be created [22]. Another example can be found in [23]. It was demonstrated that the use of a global  $N^{\text{th}}$ -order model instead of more correct autocatalytic model may result in excessive overestimation of the venting area when designing the ERS for gassy systems.



**Figure 6** Data fitting by the autocatalytic model (11a)-(11b) evaluated from the data sets A and B.  $\circ\circ\circ\circ$  - experimental points, — - simulation (1) - experiment A,  $M/A=2$ ; (2)- experiment B,  $M/A=6$

#### CHOICE OF THE METHOD FOR ESTIMATING MODEL'S PARAMETERS

Evaluation of kinetics on the basis of experimental data includes two main steps –identification of the model structure and estimation of the model's parameters (kinetic parameters).

There is no universal and well-formalized method for structure identification. Current methods depend on inspection of all the plausible models with the following selection using appropriate criterion. The estimation of a model's parameters is one of the well-developed areas of mathematics. This task requires finding estimates of the parameters that provide the best fit to experimental data. There are many alternative estimation methods, therefore, the challenge is to choose the most appropriate method that will give reliable resultant kinetics.

Consider first the mathematical model of a BATCH process, which involves a simple  $N^{\text{th}}$ -order

exothermic reaction. This model includes the kinetic equation (12a) and the heat balance equation (12b)

$$\frac{d\alpha}{dt} = k_0 e^{-\frac{E}{RT_s}} (1-\alpha)^n \quad (12a)$$

$$c_s m_s \varphi \frac{dT_s}{dt} = m_s Q^\infty \frac{d\alpha}{dt} - US(T_s - T_e) \text{ or}$$

$$T_s - T_e = \left(\frac{US}{m_s}\right)^{-1} \frac{dQ}{dt} - \left(\frac{US}{m_s}\right)^{-1} c_s \varphi \frac{dT_s}{dt} \quad (12b)$$

in addition to the corresponding initial conditions. We consider here a simple formal model, but all the results will be equally valid for kinetic models of any type and complexity.

From the formal point of view the model (12a, b) contains:

- state (dependent) variables  $\alpha$  and  $T_s$  measured with some errors in the course of an experiment (for descriptive models concentrations will appear instead of conversions);
- a control variable  $T_e$  and control parameters  $US$ ,  $\varphi$ , etc., that are known precisely,
- a set of kinetic parameters  $k_0$ ,  $E$ ,  $n$ ,  $Q^\infty$  that are subject to estimation.

There is only one independent variable – time. The non-linear equation system (12a, b) should be integrated both for simulation of a process and for kinetic parameters estimation. In the last case integration must be done dozens of times. This general approach is absolutely correct, but rather complex. In spite of its complexity, this approach is applied more and more often (see, for example, [1, 3, 6-9, 11, 13, 15]).

Nevertheless, application of simplified time-effective methods that don't involve complex calculations remains very attractive and is often applied [4, 10, 14]. Such methods should be used carefully, especially in hazard assessment area, for in many cases they may give incorrect and unsafe results. Therefore, we believe that a discussion of the basic features of these methods is appropriate.

### Simplified methods for parameters estimation

#### *Interpretation of sample temperature*

Significant simplification is achieved if sample temperature can be considered as an independent variable. In this case one has to take into account only one kinetic equation (12a) and there is no need for numerical integration of the complete model. Many methods of kinetic evaluation based on this simplifying assumption

are used very often without prior verification of its validity.

The possibility to treat the sample temperature as an independent variable strongly depends on the intensity of heat removal. Consider two cases using the modified form of the equation (12b).

1. Heat is intensively removed from a reactor (specific heat transfer  $US/m_s$  is very big) so that heat accumulation is negligible,  $T_s$  is very close to  $T_e$  ( $T_s \approx T_e$ ) and weakly depends on heat generation in the reactor. In this case, one can use  $T_e$  instead of  $T_s$  or guess that  $T_s$  is the independent variable. Such conditions are typical for small-scale laboratory reactors when the mass of a reactant is small (scanning or heat flux calorimetry with  $m_s \ll 1$  g are the examples) so that even if the heat removal  $US$  is moderate the specific heat removal term  $US/m_s$  is large enough.

2. Heat removal is tenuous. In this case, heat generation causes a deviation of  $T_s$  from  $T_e$ . The extent of this deviation depends on  $US/m_s$  and may vary from several degrees for isoperibolic mode to several tens or even hundreds of degrees for adiabatic conditions

( $US/m_s \approx 0$ ). For these types of data,  $T_s$  is principally the dependent quantity (state variable). Therefore the complete non-linear equation system (12a, b) should be used for kinetics evaluation and appropriate methods of non-linear optimization must be applied, otherwise the kinetics obtained will be incorrect.

#### *Arrhenius linearization method*

One of the most popular methods that uses the assumption about the sample temperature and conversion as the independent variables is the Arrhenius linearization method. A model is linearized with respect to the kinetic parameters by using the logarithmic transformation:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(k_0) + n \cdot \ln(1-\alpha) - \frac{E}{R} \cdot T_s^{-1} \quad (13)$$

and, if  $\alpha$ ,  $d\alpha/dt$  and  $T_s$  are known, the kinetic parameters can be estimated easily by using the linear Least Square Method (LSM).

The well-known limitation of this method is that it is applicable only to some single stage models (for instance, it doesn't allow estimation of all the parameters of the single-stage autocatalytic model (6a)). There are other limitations, including:

1. Application of the LSM requires that the degree of conversion and sample temperature are known precisely and considered as independent variables.

As conversions cannot be measured directly they should be evaluated from some measured responses. Usually conversion is calculated as the ratio of the current value of a response to its final value (e.g. ratio of the current adiabatic overheating to its maximum value in an adiabatic experiment). Therefore, an experiment must be continued until the completion of the reaction, otherwise the estimate of the conversion will be incorrect. Furthermore, the precision of the calculated conversion will depend on the precision of measurement and the features of the data; therefore, the application of conversion as an independent variable is questionable.

2. It was shown earlier that there are only a few special cases where the sample temperature can be treated as an independent variable. This cannot be done with respect to adiabatic data. Nonetheless, this assumption is often used for kinetics evaluation in adiabatic calorimetry just by tradition, having been transferred from other areas of reaction investigation.

A dramatic instance of the oversimplified approach to kinetics evaluation can be found in the recent article [14] where the global single-stage N-order model is applied in combination with the Arrhenius method to assess the apparent activation energy, whereas the adiabatic self-heating rate curve unambiguously reveals a complex multi-stage reaction.

The following example demonstrates what may happen if the sample temperature in an adiabatic experiment is interpreted as the independent variable.

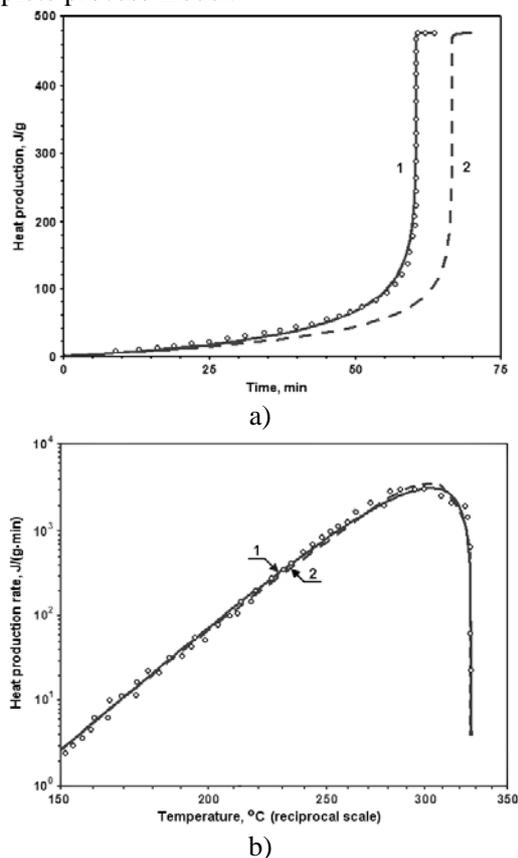
At first the kinetic parameters were estimated on the basis of adiabatic data (Figure 7) using the Arrhenius method. Due to errors in measurement the parameters were also calculated with some errors. Then the reaction course was simulated by interpreting  $T_S$  as an independent variable, that is, the experimental temperature was substituted in the kinetic equation (12a) for calculation of the rate constant. The simulated curve (Figure 7a, solid line 1) deviates only slightly from the experimental points because the calculated reaction rate differs from the true one due to error in the activation energy.

The reaction course was then simulated by numerical integration of the complete process model. Specifically,  $T_S$  was calculated from the heat balance equation (12b). The resulting curve (Figure 7a, dotted line 2) is shifted significantly compared to the experimental curve. Why did it happen?

In the first case the error in the activation energy causes only a small deviation in the reaction rate.

In the second case the same variation in the reaction rate results in a change in  $T_S$ . The variation in  $T_S$  changes the reaction rate. Because of the exponential dependency of the reaction rate on  $T_S$ , this feedback significantly magnifies the influence of the parameter errors, i.e. significant parametric sensitivity of the simulation results is observed (see [12] for more detailed consideration).

Nevertheless, it may seem that the simplified method of calculation can be applied because it gives a reasonable correspondence with the experimental results - but it would be misleading. The main purpose of simulation is to predict the reaction course under conditions of practical interest that differ from experimental conditions. Therefore, there is no other way to obtain the necessary results but to use the complete process model.



**Figure 7.** Inapplicability of the Arrhenius method for kinetics evaluation in adiabatic experiment.

○ ○ ○ ○ - experimental points, — - simulation  
 (a) heat release in the reaction course; (b) heat generation rate (Arrhenius plot). (1) - simulation based on the simplified model; (2) - simulation based on the complete model

The general approach discussed earlier considers the complete model of a process. When it is applied

to parameters estimation, the parameter's sensitivity is automatically taken into account; therefore, estimates obtained are more reliable and suitable for simulation. Examples of application of such an approach for kinetic analysis of adiabatic data can be found in [11, 13].

Attention should be given to one important feature. The temperature profiles of a reaction are alike, but shifted along the time axis with respect to one another. Therefore, the Arrhenius plot (Figure 7b) of the reaction rate versus reciprocal temperature, which is typically used for data analysis in adiabatic calorimetry, shows only a small difference between the curves. This is one of the reasons why it is hard to discover the deficiency of the Arrhenius-like methods.

### Applying non-linear optimization methods for parameters estimation

The general approach to kinetics evaluation is based on non-linear optimization. We will discuss here only the main features and some important problems dealing with application of non-linear estimation. Please refer to [1, 6-8, 24] for more details.

The aim of the estimation procedure is to find values of the parameters that ensure the best fit to the experimental data. To achieve this goal one should minimize some measure of residuals between experimental and simulated responses. The majority of non-linear optimization algorithms are based on the Least Squares Method (LSM) which uses the sum of squares of residuals as the measure. Therefore, the sought for estimate of the parameters vector  $\bar{\mathbf{P}}_r$  is determined by minimizing the objective function SS:

$$SS(\bar{\mathbf{P}}) = \frac{1}{2} \sum_{(i)} \left( \frac{Y_{\text{exp}}(t_i) - Y_{\text{sim}}(\bar{\mathbf{P}}, t_i)}{\varepsilon_i} \right)^2 \rightarrow \min = SS(\bar{\mathbf{P}}_r) \quad (14)$$

where  $SS(\bar{\mathbf{P}})$  denotes the weighted sum of the squares of the residuals;  $Y_{\text{exp}}(t_i)$  is the value of the experimental response at  $t=t_i$  (i-th experimental point);  $Y_{\text{sim}}(\bar{\mathbf{P}}, t_i)$  is the value of the simulated response at  $t=t_i$ ; ( $Y$  denotes the sample temperature, heat or gas release, concentrations, etc.);  $\varepsilon_i$  represents the experimental error for the i-th point;

The condition of the SS minimum is defined by the system of non-linear algebraic equations:

$$\partial SS(\bar{\mathbf{P}}) / \partial P_j = 0; j=1, \dots, L; \quad (15)$$

where  $P_j$  is j-th component of the parameters vector.

The objective function can be expanded to cover data of several multi-response experiments:

$$SS = \sum_{(k)} \varpi_k SS_k \rightarrow \min = SS(\bar{\mathbf{P}}_r),$$

$$SS_k = \sum_{(j)} \varpi_{kj} \sum_{(i)} \left( \frac{Y_{\text{exp}}^{kj}(t_i) - Y_{\text{sim}}^{kj}(\bar{\mathbf{P}}, t_i)}{\varepsilon_{kji}} \right)^2 \quad (16)$$

where  $SS_k$  is the objective function for the k-th data set; this accounts for the contribution of all the responses of the set,  $\varpi_k$  is its statistical weight;  $Y_{\text{exp}}^{kj}(t_i)$  is the value of the j-th response at i-th experimental point;  $Y_{\text{sim}}^{kj}(t_i)$  is the value of the j-th simulated response at  $t=t_i$ ;  $\varepsilon_{kji}$  is the experimental error for i-th point of the j-th response;  $\varpi_{kj}$  is the statistical weight of the j-th response. Moreover, the objective function can include not only responses of different physical quantities, but also integral and derivative responses of the same physical quantity.

It should be emphasized that the possibility to simultaneously treat data from several experiments and responses of a different physical nature is very important because it allows utilizing universal information about the reaction, thus providing more adequate resulting kinetics.

For a non-linear kinetic function  $Y_{\text{sim}}(\bar{\mathbf{P}}, t)$  the system (15) is non-linear and can be solved only numerically. It represents a very difficult mathematical problem. Therefore, non-linear optimization is usually applied. A multitude of methods of this kind have been created so that there is no need to develop any new methods – the problem is to choose the most appropriate from the existing ones that would satisfy the problem features.

#### Constraints on the parameters.

The problem (16) represents the absolute extreme problem when the minimum is sought through the whole domain of parameters. It may result in very time consuming calculations and finding the formal solution with the parameters that don't have any physical sense. Therefore the optimization method must allow imposing the constraints on the parameters to limit their tolerance range:

$$P_j^{\min} \leq P_j \leq P_j^{\max} \quad (17)$$

Some other constraints that bound one or another group of parameters may be useful as well. For example, sometimes it is expedient to demand that activation energies of some stages of the multi stage model be equal to each other.

### *Choice of the initial guess.*

Non-linear optimization requires assignment of the initial guess on parameters, which is different from linear estimation. The effectiveness of the parameter estimation depends highly on the location of the initial guess on the surface of the objective function SS representing dependence of the SS on parameters.

If the initial guess is located far from the minimum, and the surface is flat, it is difficult to find the true direction to the minimum. Quite the contrary, if the initial guess had been selected successfully, the direction can be determined easily and the solution will be found quickly. The “ideal” optimization method should be equally capable to start from the “bad” initial point and to find the precise position of the minimum. In practice, several mutually complimentary methods must be applied: one of them should easily detect proper direction to the minimum from the initial point; the other one should be efficient near the minimum.

### *Non-uniqueness.*

If experimental data were measured without errors, and the reaction model were exact, the estimation problem would always have a unique solution. In reality, data are measured with some error and some approximate models are used. It may result in the appearance of several local extremes instead of one global extremum; that is, the solution turns out to be non-unique.

The non-uniqueness cannot be predicted *a priori*. The only method that reveals the non-uniqueness is by scanning the domain of parameters definition; that is, estimating the parameters starting from different initial guesses. If several extremes are found, then the parameters vector that corresponds to the minimal value of the objective function should be taken as the final solution.

### **Overview of two efficient optimization methods**

Two optimization methods demonstrate their efficiency for application to kinetics evaluation and can be recommended for use. They are the modified Newton-Gauss method [25, 26] and the Tensor method [27, 28]. Both of these are based on linearization of the SS function by applying expansion in the Taylor series with the following iterative solution of the optimization problem (16) where the Taylor series substitutes for the original SS function. On every step the corrections vector is calculated followed by determination of the new estimate of the parameters vector.

The Newton-Gauss method uses only the two highest terms of the Taylor series. A good approximation of SS occurs if the expansion is made in the vicinity of the solution. Therefore, the Newton-Gauss method demonstrates fast convergence to the minimum and ensures

efficient and accurate estimates of the parameters if the initial guess is reasonably close to the sought for vector. Otherwise, the method may fail in detecting the true direction to the minimum.

The Tensor method uses the three highest terms of the Taylor series. It results in much better detection of the descent direction and, hence, in a more successful start of optimization even from a rough initial guess of the parameters. In some cases this method is less efficient in the vicinity of the minimum (requires more iterations and results in less precise estimates). Therefore, these methods represent a good example of mutually complimentary ones.

An important advantage of both these methods is that they allow imposing linear constraints to limit the tolerance range of the parameters. In addition, the Tensor method allows applying more complex constraints of the inequality type on the combinations of the parameters.

### **General features of kinetics evaluation using non-linear optimization**

The general approach to kinetics evaluation based on integration of the complete reactor model in combination with non-linear methods for estimation of the model parameters has numerous advantages, specifically:

- it is applicable to various classes of kinetic models of any complexity;
- it allows simultaneous use of several data sets obtained at various thermal modes and even by using different types of experimental methods;
- it results in more reliable estimates of the kinetic parameters even in extreme cases.

The main problem that impedes application of the approach is its complexity – it cannot be used without specialized software. There are several commercial codes that employ this approach (the Rate code developed by BatchCad [8], NETCH kinetics software [6] and some others). The ForK and DesK program packages developed by ChemInform Ltd., are other instances. Specifically, all the examples presented in the paper were obtained by applying these packages.

### **CONCLUSIONS**

Design of reaction kinetics is a complex multifaceted problem. Its solution requires a deep understanding of chemical kinetics and the experimental methods to produce the data, understanding of the mathematical aspects of reaction kinetics, and a clear understanding of how the resulting kinetic model will be applied. Many of the required steps cannot be

completely formalized, so the mathematical methods should be combined with experience and intuition of a researcher.

One of the key stages in kinetic model creation is the choice of the most appropriate model type. It has been shown that only the proper implementation of this stage can guarantee correctness of the results. Very often, additional data may be required for validation or selection of a model. Therefore, one must perform additional experiments to get the required data. Thus, in practice, kinetics evaluation is an iterative procedure.

The validity of results obtained in one step affects the results in subsequent steps. Thus, every step should be given the required attention and effort.

#### NOMENCLATURE

t – time; s  
 r – rate of a stage; s<sup>-1</sup>  
 k – rate constant of a reaction or stage; s<sup>-1</sup>  
 k<sub>0</sub> – pre-exponential factor;  
 E – activation energy; kJ/mol  
 n – reaction order;  
 z – autocatalytic constant;  
 f(α) – kinetic function, defines dependency of reaction rate on the conversion;  
 m – mass; kg  
 R – gas constant; J/(mol\*K)  
 T – temperature; K  
 Q – specific heat generation; kJ/kg, kJ/mol  
 G – specific gas generation; mol/kg, mol/mol  
 Q<sup>∞</sup> – specific heat of a reaction or stage; kJ/kg, kJ/mol  
 G<sup>∞</sup> – specific gas generation of a reaction or stage; mol/kg, mol/mol  
 Y(t) – response of a reacting system;  
 Y<sub>exp</sub> – experimental response;  
 Y<sub>sim</sub> – simulated response  
 $\bar{\mathbf{P}}$  – vector of kinetic parameters of a reaction model;  $\bar{\mathbf{P}} = \{k_0, E, n, Q^\infty, \dots\}$   
 c<sub>p</sub> – specific heat of a substance; J/(kg\*K)  
 v, β – stoichiometric coefficients;  
 α, γ – degree of conversion; 0 < α, γ < 1  
 [A] – concentration of A species, mol/m<sup>3</sup>  
 φ – heat inertia of the calorimetric cell (phi-factor);  $\phi = 1 + \frac{c_b m_b}{c_s m_s}$   
 U – heat transfer coefficient; W/(m<sup>2</sup> K)  
 S – surface of heat exchange, m<sup>2</sup>  
 Indices:  
 e – environment

o – initial value of a variable  
 s – sample  
 b – calorimetric cell  
 onset – conditions at the beginning of adiabatic mode in adiabatic calorimetry.

#### LITERATURE CITED

1. H. Anderson, A. Kemmler and R. Strey, Comparison of different non-linear evaluation methods in thermal analysis. *Thermochimica Acta*, 271 (1996), 23-29
2. M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyne, Chao-Rui Li, Tong B. Tang, B. Roduit, J. Malek and T. Mitsuhashi. Computational aspects of kinetic analysis: Part A: The ICTAC kinetics project-data, methods and results, *Thermochimica Acta*, 355 (2000) 125-143
3. M. Maciejewski, Computational aspects of kinetic analysis.: Part B: The ICTAC Kinetics Project — the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield, *Thermochimica Acta*, 355 (2000) 145-154
4. S. Vyazovkin, Computational aspects of kinetic analysis.: Part C. The ICTAC Kinetics Project — the light at the end of the tunnel?, *Thermochimica Acta*, 355 (2000) 155-163
5. A. Burnham, Computational aspects of kinetic analysis.: Part D: The ICTAC kinetics project — multi-thermal-history model-fitting methods and their relation to isoconversional methods, *Thermochimica Acta*, 355 (2000) 165-170
6. H-J. Flammersheim and J. R. Opfermann, Kinetic evaluation of DSC curves for reacting systems with variable stoichiometric compositions, *Thermochimica Acta*, 388 (2002) 389-400
7. V. G. Gorsky, Planning of the kinetic experiments, Nauka, Moscow, 1984 (in Russian)
8. A.R. Wright and V.J. Bramfit, Automation of kinetic fitting and its application in batch process scale up, Proceedings of the Personal Computing in the Process Industries Conference (PCIII), 30<sup>th</sup> November (1994)
9. M. Mehrvar et al., Non-linear parameter estimation for a dynamic model in photocatalytic reaction engineering, *Chemical Engineering Science*, v. 55, 21 (2000), 4885-4891

10. M. Ahmed, H.G. Fisher and A.M. Janeshek, Reaction kinetics from self-heat data - correction for the depletion of sample, Proceedings of the International Symposium on Runaway Reactions, Cambridge, Massachusetts (1989) 331-336.
11. H. Anderson and J. Mentel, Adiabatic decomposition kinetics by non-linear optimization, *Journal of Thermal Analysis*, 41 (1994) 471-481
12. A. Kossoy and E. Koludarova, Specific features of kinetics evaluation in calorimetric studies of runaway reactions. *J. Loss Prev. Process Ind.*, v.8, N.4, (1995) 229-235.
13. Y. Iizuka and M. Surianarayanan, Comprehensive Kinetic Model for Adiabatic Decomposition of Di-tert-butyl Peroxide Using BatchCAD, *Ind. Eng. Chem. Res.*, 42 (2003) 2987-2995
14. H. Fauske, Managing Chemical Reactivity - Minimum Best Practice, *Process Safety Progress*, 25 (2006), 120-129
15. M. Coupin Sola, Comparison of different thermal kinetic estimation methods using the reaction of acetic anhydride with methanol, BS Diploma, Universitat Ramon Llull, 2004
16. A. Kossoy, A. Benin and Yu. Akhmetshin. An Advanced Approach to Reactivity Rating, *Journal of Hazardous Materials*, v. 118, N 1-3, (2005) 9-17
17. J.A. Hare, Problem Specification for Round Robin on Chemical Reactor Relief System Models (Vapor Pressure System), Health and Safety Executive, England, 1999
18. E.C. Carlson, Don't gamble with physical properties for simulations, *Chemical Engineering Progress*, v.92, 10 (1996) 35-46
19. E. Wilcock and R.L. Rogers, A review of the phi factor during runaway conditions, *J. Loss Prev. Process Ind*, v.10, 5-6, (1997) 289-302
20. R. Widell and H. Karlsson, Autocatalytic Behavior in Esterification between Anhydrides and Alcohols, *Thermochimica Acta*, 447 (2006), 57-63
21. G. Wehmeier, Theoretische und experimentelle Untersuchung der Vorgänge bei der Druckentlastung von Chemiereaktoren, Ph.D. Dissertation. Universität Dortmund, VDI-Fortschr.-Ber. Reihe 3, Nr. 373, 1994
22. A.G. Merzanov and F.I. Dubovitski, Quasi-stationary theory of thermal explosion of self-accelerating reactions, *J. Phys. Chem.* v. 34, 10, (1960) 2235-2243 (in Russian)
23. R. Rota, G. Ruggeri, M. Morbidelli and S. Ditali, Influence of calorimetric approximations on the design of emergency relief systems, *J. Loss Prev. Process Ind*, 15 (2002) 49-61
24. D. Himmelblau, *Applied Nonlinear Programming*, McGraw-Hill, New York, 1972
25. H.O. Hartley, The modified Gauss - Newton method for fitting of nonlinear regression functions by least squares. *Technometrics*, 3, (1961), 269-280.
26. S.N. Dymov, V.S. Kurbatov, I.N. Silin and S.V. Yaschenko, Constrained minimization in the C++ environment, *Nuclear Instruments and Methods in Physics Research, Section A*, v. 440, N 2, (2000), 431-437
27. R J Hanson, Least Squares with Bounds and Linear Constraints, *SIAM Journal of Scientific and Statistical Computing*, v. 7, N 3, (1986), 826-834.
28. R Schnabel, P Frank, Tensor Methods for Nonlinear Equations, *SIAM Journal on Numerical Analysis*, v. 21, N 5, (1984), 815-843.