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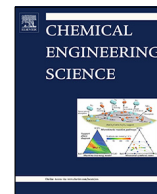
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# Determination of kinetic constants by using transient temperature data from continuous stirred tank reactors



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## ABSTRACT

Mathematical modelling of transient states of continuous stirred tank reactors was considered for the case of homogeneous liquid-phase reactions. A simple and very precise kinetic measurement strategy was proposed: registration of the reactor temperature during the start-up of the reaction process. The dynamic reactor model consisted of mass and energy balances written in dimensionless forms to enable general conclusions and easy computer implementation. Model simulations were carried out by using a numerical solver for stiff differential equations and a reaction invariant was revealed by theoretical analysis. A series of transient laboratory-scale experiments for a strongly exothermic reaction, a reaction between sodium thiosulphate and hydrogen peroxide was conducted and the kinetic parameters, the pre-exponential factors and activation energies were estimated. The data fitting was further improved by incorporating the decomposition of hydrogen peroxide as a side reaction. The estimated kinetic parameters were investigated further by sensitivity analysis and Markov-Chain-Monte-Carlo-Method (MCMC) to confirm their reliability. The proposed method is applicable for relatively simple systems with a measurable heat effect. For complex multireaction systems the method should be completed with chemical analysis.

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## 1. Introduction

Precise kinetic measurements are extremely important both from the viewpoint of fundamental science and applied engineering. Kinetic measurements give valuable information about the underlying reaction mechanisms and rival mechanistic assumptions can be compared by using experimentally recorded kinetic data and rate equations based on presumed molecular mechanisms. Kinetic models have a huge practical impact on the design of chemical reactors in industrial scale: the reaction rates have a strong influence on the mass and energy balances used in contemporary analysis, design and optimization of chemical reactors. In field of reaction kinetics, the fundamental and applied aspects live in a beautiful and useful co-existence.

There are however bottle-necks in the kinetic research work. The obstacles are often coupled to cumbersome chemical analysis consisting of sampling, reaction quenching and sample pre-treatment such as derivatisation. On line analysis methods such as in situ spectroscopy, conductometry, pH measurement and

selective electrodes are of great help if they can be implemented in the system under investigation. This is not always possible. A simple measurement is always very attractive; if the reaction has a measurable heat effect, if the reaction is exothermic or endothermic: recording of the reaction temperature during the experiment gives very valuable kinetic and thermodynamic information. Temperature measurements with thermocouples and optical fibres are nowadays very precise, the accuracy being typically around 0.1 °C and response of the temperature sensor is very rapid. The classical way of thinking advices to strive isothermal conditions in kinetic experiments, but changing the temperature by purpose gives valuable information about the temperature dependence of the rate constant. Calorimetric work is well-established to determine reaction enthalpies and it can be combined with non-isothermal experiments (Salmi et al 2019).

Several studies have shown the benefits of using reaction temperature or heat-flow rate (calculated from the reaction temperature derivative) to estimate kinetic constants (e.g. Dobrosavljevic et al 2016, Hoffmann et al. 2007, Marco et al. 2000, Snee et al. 1993, Todd and Gomez, 2001, Vernières-Hassimi et al. 2017, Zogg et al. 2004). One should keep in mind the requirements of this attractive method: an appropriate thermal characterization of the

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## Nomenclature

$C$	dimensionless concentration	$\beta$	parameter in reaction invariant
$C'$	heat capacity of the reactor vessel	$\theta$	transformed temperature
$c$	concentration	$\nu$	stoichiometric coefficient
$c_p, c_v$	specific heat capacities	$\rho$	density
$D$	degree of explanation	$\tau$	space time (residence time)
$E_a$	activation energy		
$\Delta H$	reaction enthalpy		
$k$	reaction rate constant		
$m'$	mass flow		
$n$	amount of substance		
$n'$	flow of amount of substance, molar flow		
$Q$	residual sum of squares, objective function		
$R$	reaction rate		
$R_G$	general gas constant, 8.3143 J/(K mol)		
$r$	component generation rate		
$T$	temperature		
$t$	time		
$U$	internal energy		
$V$	volume		
$V'$	volumetric flow rate		
$y$	reaction invariant		
$\alpha$	parameter in reaction invariant		

### Subscripts and superscripts

exp	experimentally observed quantity
i	component index
j	reaction index
ref	reference
0	inlet or initial quantity

### Abbreviations

A	thiosulphate $S_2O_3^{2-}$
B	hydrogen peroxide $H_2O_2$
R	$S_3O_6^{2-}$
S	sulphate $SO_4^{2-}$
O	oxygen $O_2$
W	water $H_2O$

chemical reactor (heat-exchange coefficient, specific heat capacity, heat loss) and the knowledge of reaction, mixing and solubilization enthalpies. The latter condition is compulsory in the case of multiple reactions. By using transient experiments in continuous reactors and measuring the temperature change as a function of time enables screening of large temperature intervals with few experiments. The use of a continuous reactor with a well-defined flow pattern is a necessity for successful non-isothermal transient experiments. In a recent work carried out in Magdeburg (Bremer 2020), the use of continuous non-isothermal fixed beds for transient experiments of the Sabatier reaction was successfully demonstrated: the rate parameters were determined with very precise temperature measurements. Garcia-Hernandez et al. (2019) studied successfully the reaction kinetics of acetic anhydride hydrolysis by utilizing temperature measurements.

In the present work, we survey the theory for non-isothermal liquid-phase experiments in continuous stirred tank reactors (CSTR) and demonstrate the concept with a strongly exothermic model reaction between sodium thiosulphate and hydrogen peroxide. The oxidation of sodium thiosulfate is a typical test reaction used to evaluate the reliability of a calorimeter and to study the stability and steady state multiplicity of a CSTR (Root and Schmitz, 1969, Vejtasa and Schmitz 1970, Chang et al. 1975). The kinetics of this reaction system has been investigated in batch mode (Grau et al. 2000) and in CSTR under steady state conditions (Vejtasa and Schmitz 1970). Guha et al. (1975) studied this system in a dynamic CSTR under adiabatic conditions but did not include a parameter estimation stage.

## 2. Modelling of adiabatic CSTR under transient conditions

### 2.1. Fundamental model hypotheses

An adiabatically operated continuous stirred tank reactor (CSTR) is considered under transient conditions. The reactor vessel is well-isolated so the heat transfer through the reactor walls is negligible. The only heat exchange with the outer environment takes place through the inlet flow of the reactant solution. Further-

more, because of vigorous agitation neither temperature nor concentration gradients appear inside the reactor vessel. Liquid-phase reactions are assumed to proceed either spontaneously or in the presence of a fully miscible homogeneous catalyst. The physical properties, such as the liquid-phase heat capacity and density are approximated to be constant. A principal sketch of the reactor system is provided in Fig. 1.

### 2.2. Mass and energy balances

The primary form of the mass balance for an arbitrary, reactive component ( $i$ ) in a perfectly mixed CSTR can be written as

$$n'_{0i} + \sum v_{ij}R_jV = n'_i + \frac{dn_i}{dt} \quad (1)$$

The symbols are listed in Notation. After introducing the definitions of concentrations ( $c_i$ ), the amount of substance ( $n_i = c_iV$ ) as well as the molar flows ( $n'_i = c_iV'$ ) and the space time ( $\tau = V/V'$ ) in the balance equation (1), an operative form is obtained,

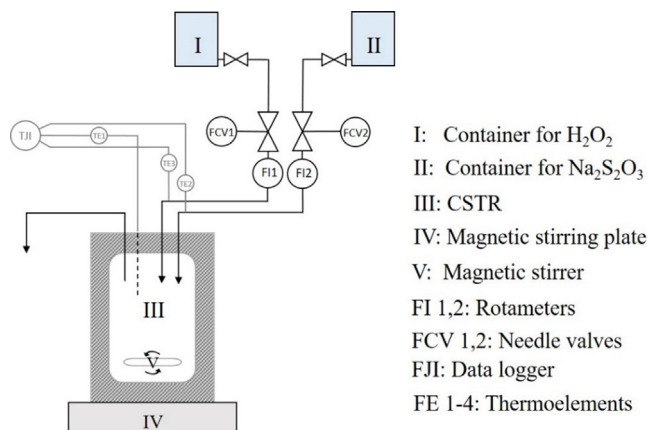


Fig. 1. A principal sketch of an adiabatically operated CSTR.

$$\frac{dc_i}{dt} = \frac{c_{0i} - c_i}{\tau} + \sum v_{ij}R_j \quad (2)$$

The initial condition is  $c_i = c_i(0)$  at  $t = 0$ .

The energy balance for the adiabatic CSTR can be written as

$$m' \int_{T_{ref}}^{T_0} c_p dT + \sum (-\Delta H_j R_j) V = m' \int_{T_{ref}}^T c_p dT + \frac{dU}{dt} \quad (3)$$

The term  $dU/dt$  consists in principle of two contributions, the change of the internal energy of the liquid phase and the heat capacity of the reactor vessel:  $dU/dt = (mc_v + C')dT/dt$ . In case that the heat capacity of the reactor vessel can be neglected,  $C' \rightarrow 0$ . For liquid-phase processes, the heat capacities at constant pressure ( $c_p$ ) and constant volume ( $c_v$ ) can be approximated equal (Reid et al. 1988). After introducing these concepts and assuming that the heat capacity is independent of temperature, the energy balance (3) takes the operative form

$$\frac{dT}{dt} = \frac{T_0 - T}{\tau} + \frac{\sum (-\Delta H_j R_j)}{c_p \rho_0} \quad (4)$$

The initial condition is  $T = T(0)$  at  $t = 0$ .

For theoretical and numerical considerations it is practical to transfer the mass and energy balances to fully dimensionless forms. Dimensionless concentrations ( $C$ ) are introduced by the definition  $C_i = c_i/c_{0A}$ , where  $c_{0A}$  is the concentration of the reference (key) component (A) in the inlet flow. The dimensionless time is defined by  $\theta = t/\tau$ , where  $\tau$  is the space time,  $\tau = V/V'$ . After introducing the dimensionless quantities, the mass and energy balances become

$$\frac{dC_i}{d\theta} = C_{0i} - C_i + \frac{\sum v_{ij}R_j\tau}{c_{0A}} \quad (5)$$

$$\frac{d(T/T_0)}{d\theta} = 1 - T/T_0 + \frac{\sum (-\Delta H_j R_j)\tau}{c_p \rho_0 T_0} \quad (6)$$

The following initial conditions are valid at  $t = 0$ :

$$C_i = C_i(0) \quad (7)$$

$$T/T_0 = T(0)/T_0 \quad (8)$$

A further analysis of the mathematical model depends on the particular reaction kinetics under consideration, i.e. the mathematical expressions for the reaction rates ( $R_j$ ).

For single reaction systems ( $A =$  key reactant) the balance equations (5)-(6) are simplified to

$$\frac{dC_A}{d\theta} = 1 - C_A + \frac{v_A R \tau}{c_{0A}} \quad (9)$$

$$\frac{d(T/T_0)}{d\theta} = 1 - T/T_0 + \frac{(-\Delta HR)\tau}{c_p \rho_0 T_0} \quad (10)$$

The reaction rate can be eliminated from the above equation by a simple algebraic trick. The parameters  $\alpha = -v_A \tau / c_{0A}$  and  $\beta = -\Delta H \tau / (c_p \rho_0 T_0)$  are introduced and equations (9)-(10) take the forms

$$\frac{dC_A}{d\theta} = 1 - C_A - \alpha R \quad (11)$$

$$\frac{d(T/T_0)}{d\theta} = 1 - T/T_0 + \beta R \quad (12)$$

Addition of the equations gives

$$\beta \frac{dC_A}{d\theta} + \alpha \frac{d(T/T_0)}{d\theta} = \alpha + \beta - \beta C_A - \alpha(T/T_0) \quad (13)$$

which means that a reaction invariant ( $y$ ) has been discovered:

$$y = \beta C_A + \alpha(T/T_0) \quad (14)$$

A very simple linear differential equation

$$\frac{dy}{d\theta} = \alpha + \beta - y \quad (15)$$

is obtained and it can be solved analytically by separation of variables and integration. The result is

$$y = \alpha + \beta - (\alpha + \beta - y(0))e^{-\theta} \quad (16)$$

Equation (16) implies that a linear combination of the dimensionless key component concentration ( $C_A$ ) and dimensionless temperature ( $T/T_0$ ) follows a simple exponential function which is valid for all single-reaction systems and completely independent of the particular reaction kinetics. Equation (16) can be used to check whether the hypothesis of complete backmixing is valid for the stirred tank reactor and no separate measurements with inert tracers are needed.

Alternatively, heat can be used as a tracer. For instance, if the reactor is initially filled with a cold solvent and a feed of hot solvent is switched on under reaction-free conditions, the temperature response is given by the differential equation (12) ( $R = 0$ ) which has the analytical solution

$$T = T_0 - (T_0 - T(0))e^{-t/\tau} \quad (17)$$

where  $T_0$  is the inlet temperature of the hot solvent and  $T(0)$  is the initial temperature of the cold solvent in the reactor. If perfect backmixing prevails in the adiabatic reactor vessel, equation (16) is valid and the mean residence time ( $\tau$ ) can be determined by regression analysis from experimental temperature data ( $T$  versus  $t$ ). Equation (17) can be used in the logarithmic form to check the flow pattern:

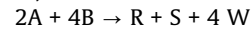
$$-\ln \left[ \frac{T_0 - T}{T_0 - T(0)} \right] = \frac{t}{\tau} \quad (18)$$

i.e. the logarithm on the left-hand side vs. the time should give a straight line for a CSTR, the slope being  $1/\tau$ .

### 3. Illustration example

An experiment was carried out by feeding hot water to the adiabatic tank reactor (Fig. 1) which was originally filled with water at room temperature. The step response of the reactor temperature and the corresponding logarithmic plot (Eq. (18)) are displayed in Fig. 2. The plot is linear confirming complete backmixing in the reactor vessel.

The method of determining rate constants is illustrated with the well-known strongly exothermic reaction between sodium thiosulphate (A) and hydrogen peroxide (B) (Vejtasa and Schmitz 1970). The reaction stoichiometry is given below,



where  $A = S_2O_3^{2-}$ ,  $B = H_2O_2$ ,  $R = S_3O_6^{2-}$ ,  $S = SO_4^{2-}$  and  $W = H_2O$ .

It is generally believed that the system follows irreversible second-order kinetics

$$R = kC_A C_B = kC_A C_B c_{0A}^2 \quad (19)$$

The rate constant is assumed to obey the law of Arrhenius,

$$k = k_0 e^{-(E_a/RG)(1/T - 1/T_{mean})} \quad (20)$$

The modified form of the original Arrhenius equation is used to suppress the mutual correlation between the pre-exponential factor and the activation energy. Parameter  $k_0$  represents in fact the value of the rate constant at the reference temperature.

The reactor system is displayed in Fig. 1 and the numerical values of the experimental parameters are listed in Table 1. For sodium thiosulphate (A) and hydrogen peroxide (B) the mass balances

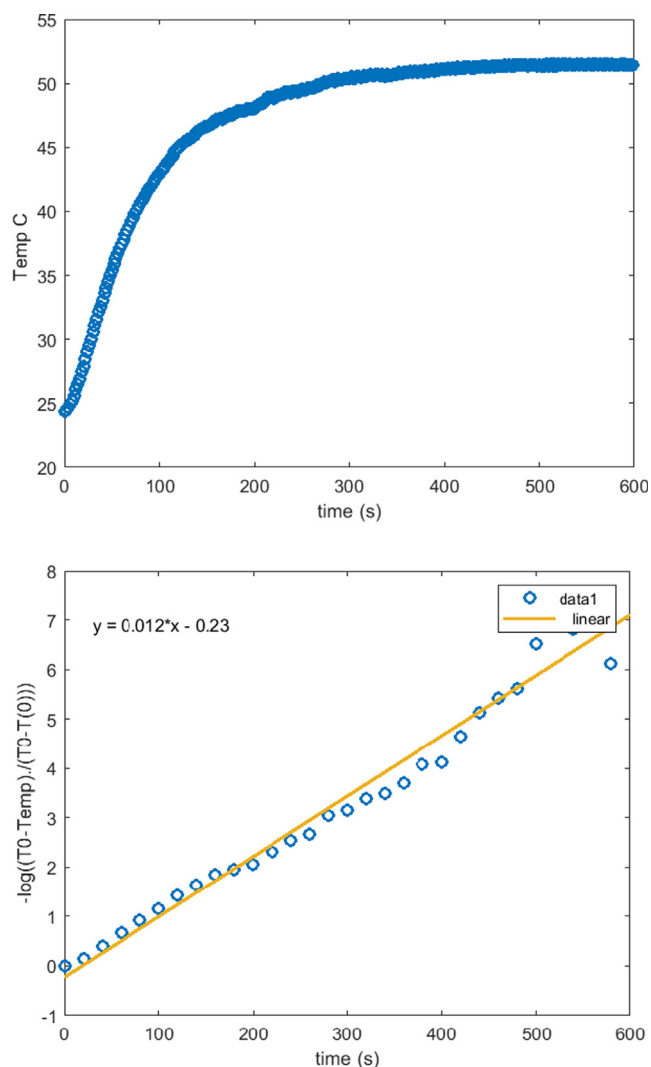


Fig. 2. Test of the flow pattern of the tank reactor: original data (upper) and logarithmic transformation of the data (lower).

$$\frac{dC_A}{d\theta} = 1 - C_A - \alpha_A R \quad (21)$$

$$\frac{dC_B}{d\theta} = C_{OB} - C_B - \alpha_B R \quad (22)$$

are used together with the dimensionless energy balance, equation (12). It should be observed that  $C_{OB} = c_{OB}/c_{OA}$  in equation (22). Parameters  $\alpha_A$  and  $\alpha_B$  are  $\alpha_A = -v_A\tau/c_{OA}$  and  $\alpha_B = -v_B\tau/c_{OA}$ .

The differential equation system was solved numerically during the parameter estimation by using the backward difference method implemented in the software package ModEst (Haario 2011). The objective function ( $Q$ ) for the parameter estimation was formulated in a very simple way,

$$Q = \sum (T_{k,\text{exp}} - T_k)^2 \quad (23)$$

where the subscript  $k$  refers to the temperature at a time point  $t$ ;  $T_k$  was computed from the model equations (12), (21) and (22).

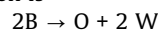
All the experimental temperature measurements were given equal weights. The minimization of the objective function was commenced with the simplex method, but as the minimum was approached, the algorithm was switched to the more rapid Levenberg-Marquardt method. The procedure was finalized with sensitivity analysis and MCMC analysis (Alcazar and Ancheyta 2007, Félix et al., 2019, Haario et al. 2001, 2006). In the sensitivity analysis, the value of the objective function was calculated after perturbation of the values of individual parameters and the change of the objective function was monitored. The MCMC method gave probabilistic distributions of the parameters. Both methods were used to investigate whether a global minimum of the objective function had been achieved.

The overall degree of the explanation ( $D$ ) was checked with the formula

$$D = 1 - \frac{\sum (T_{k,\text{exp}} - T_k)^2}{\sum (T_{k,\text{exp}} - T_{\text{mean}})^2} \quad (24)$$

where  $T_{\text{mean}}$  is the mean value of all experimental temperatures. Values of  $D$  close to 1 imply that the model is superior to the simplest possible model represented by the mean value of the experimental data.

The first parameter estimation results are collected in Table 2 and displayed in the graphs in Fig. 3. A general conclusion is that the model gives a description of the experimentally recorded transient temperature responses with quite good parameter estimation statistics. However, a principal discrepancy remains: the experimental curve is bending in a softer way than the model prediction. This systematic deviation was confirmed with several experiments and corresponding parameter estimations. – What could be the explanation? Our first hypothesis was that the reactor was not fully adiabatic, but an addition of a heat transfer term to the energy balance did not improve the model fit. The main reason of the discrepancy was revealed to be coupled to the considerable temperature increase during the experiment: the reactor temperature increases from room temperature to approx. 50–70 °C. It is well-known that the decomposition of hydrogen peroxide is strongly promoted by temperature: at room temperature the decomposition is extremely slow, but it accelerates quickly as the temperature increases or impurities are present in the system (Laidler 1987, Pędziwiatr et al. 2018). The stoichiometry of the decomposition is



where B = hydrogen peroxide, O = oxygen and W = water.

Therefore, the decomposition of hydrogen peroxide was included in the model. Irreversible first-order kinetics was assumed for the decomposition. The improved kinetic model became  $r_B = v_B R - k_B C_B$ , where  $k_B$  is the rate constant for hydrogen peroxide decomposition. This rate constant was presumed to follow the exponential temperature dependence according to the Arrhenius law.

Table 1

List of experimental parameters.

Liquid volume in the reactor: 110 mL
Volumetric flow rates of sodium thiosulphate and hydrogen peroxide: 93 mL/min
Inlet concentrations of sodium thiosulphate and hydrogen peroxide: 0.67 and 1.29 mol L <sup>-1</sup>
Inlet temperatures of sodium thiosulphate and hydrogen peroxide solutions: 22.3 °C
Mean temperature $T_{\text{mean}} = 45$ °C
Parameter $c_p\rho_0 = 4180$ J L <sup>-1</sup> K <sup>-1</sup>

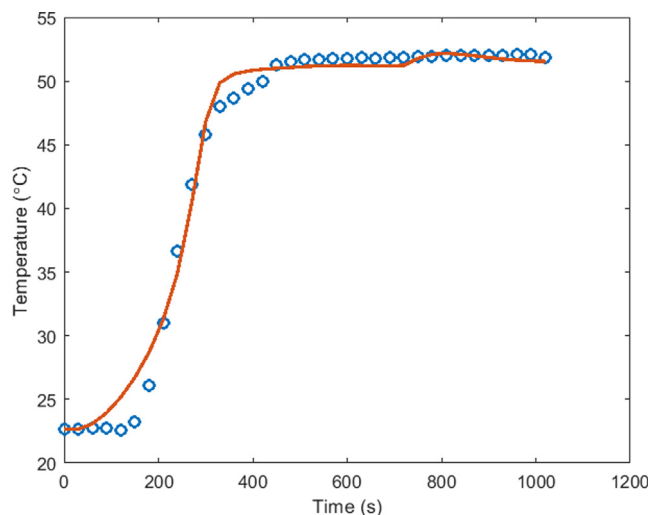


Fig. 3. Comparison of model fit to experimental data: initial model.

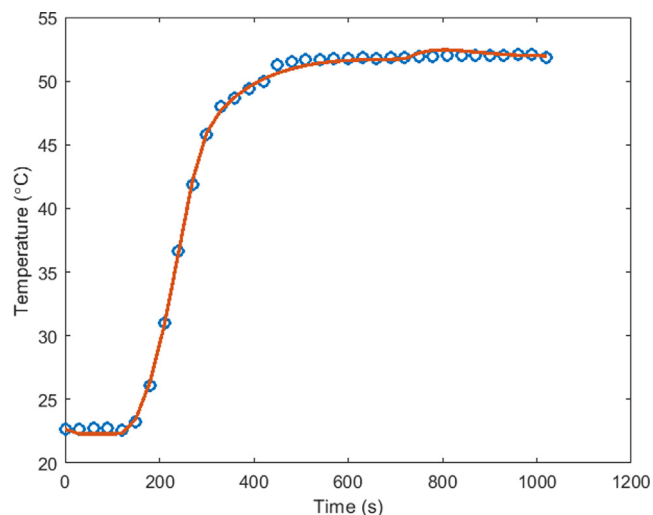


Fig. 4. Comparison of model fit to experimental data: improved model including hydrogen peroxide decomposition.

The parameter estimation procedure was repeated with the improved model. The results are collected in Table 3 and the fit of the model to the data is illustrated in Fig. 4. Principally similar transient data were obtained for different initial and inlet conditions. In this case, the matter was balancing between a high enough temperature rise to obtain the activation energy of the main reaction, but simultaneously keep the side reaction, the hydrogen peroxide decomposition under control.

A perfect description of the experimental observations was achieved and also the estimation statistics was very satisfactory. The degree of explanation exceeded 99%. The mutual correlations and the parameter sensitivities were investigated with classical sensitivity analysis and in more detail with MCMC analysis as

reported in Figs. 5 and 6. The sensitivity plots displayed in Fig. 5 confirm that the parameter minima are rather well defined. The correlations between most parameters are on a reasonable level, except the one between the activation energies for the main and the side reaction; in fact, the activation energies of both reactions are very close to each other, about 70 kJ/mol, which is also confirmed by the sensitivity plots obtained from the MCMC analysis (Fig. 5). For the hydrogen peroxide decomposition in the absence of catalysts an activation energy of 70 kJ/mol has been reported previously (Laidler 1987), which means that an increase of the temperature from 20 °C to 50 °C increases the decomposition rate with a factor of 14.4.

Table 2

First parameter estimation results (decomposition of H<sub>2</sub>O<sub>2</sub> neglected).

	Parameter	Error	Error(%)
$k_{01}$ (Lmol <sup>-1</sup> s <sup>-1</sup> )	0.498E-01	0.899E-02	18.0
$E_{a1}$ (Jmol <sup>-1</sup> )	0.133E + 06	0.784E + 04	5.9
$-\Delta H_1$ (Jmol <sup>-1</sup> )	0.467E + 06	0.117E + 05	2.5
Correlation matrix of the parameters			
$k_{01}$	1.000		
$E_{a1}$	0.994	1.000	
$\Delta H_1$	0.9850.969	1.000	
$D = 0.9884$			

Table 3

Improved parameter estimation results (decomposition of H<sub>2</sub>O<sub>2</sub> included).

	Parameter	Error	Error(%)
$k_{01}$ (Lmol <sup>-1</sup> s <sup>-1</sup> )	0.371E-02	0.128E-02	34.4
$k_{02}$ (s <sup>-1</sup> )*	0.249E-01	0.958E-02	38.4
$E_{a1}$ (Jmol <sup>-1</sup> )	0.717E + 05	0.121E + 05	16.9
$E_{a2}$ (Jmol <sup>-1</sup> )*	0.705E + 05	0.127E + 05	18.1
$-\Delta H_1$ (Jmol <sup>-1</sup> )	0.199E + 08	0.815E + 07	41.0
$\Delta H_2$ (Jmol <sup>-1</sup> )	0.149E + 07	0.520E + 06	34.9
Correlation matrix of the parameters			
$k_{01}$	1.000		
$k_{02}$	-0.583	1.000	
$E_{a1}$	-0.308	0.931	1.000
$E_{a2}$	-0.384	0.956	0.997
$\Delta H_1$	0.953	-0.615	-0.312
$\Delta H_2$	0.388	-0.898	-0.952
$D = 0.9989$			
*) Decomposition of H <sub>2</sub> O <sub>2</sub>			

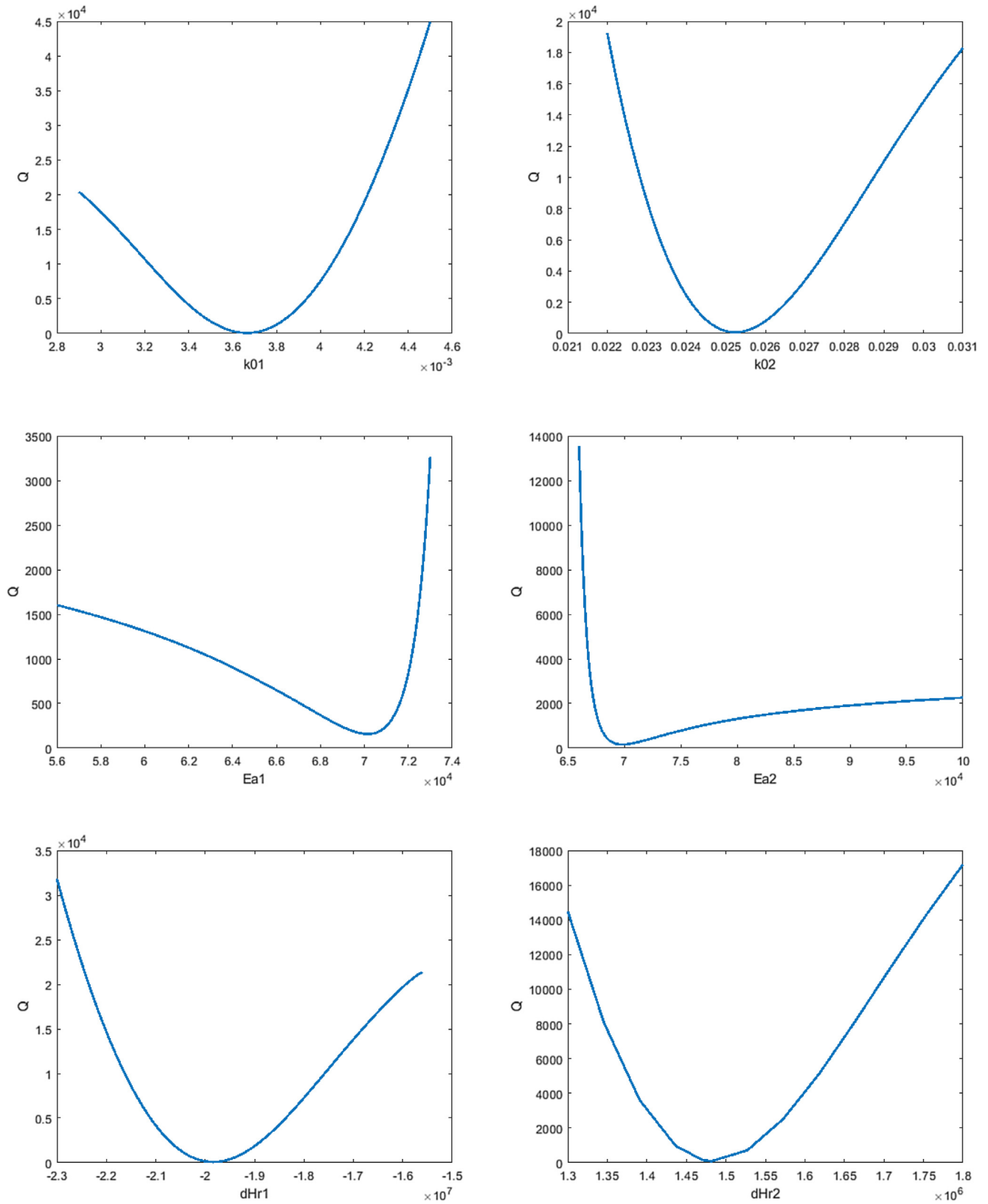


Fig. 5. Sensitivity plots of the parameters: objective function ( $Q$ ) as a function of individual parameters.

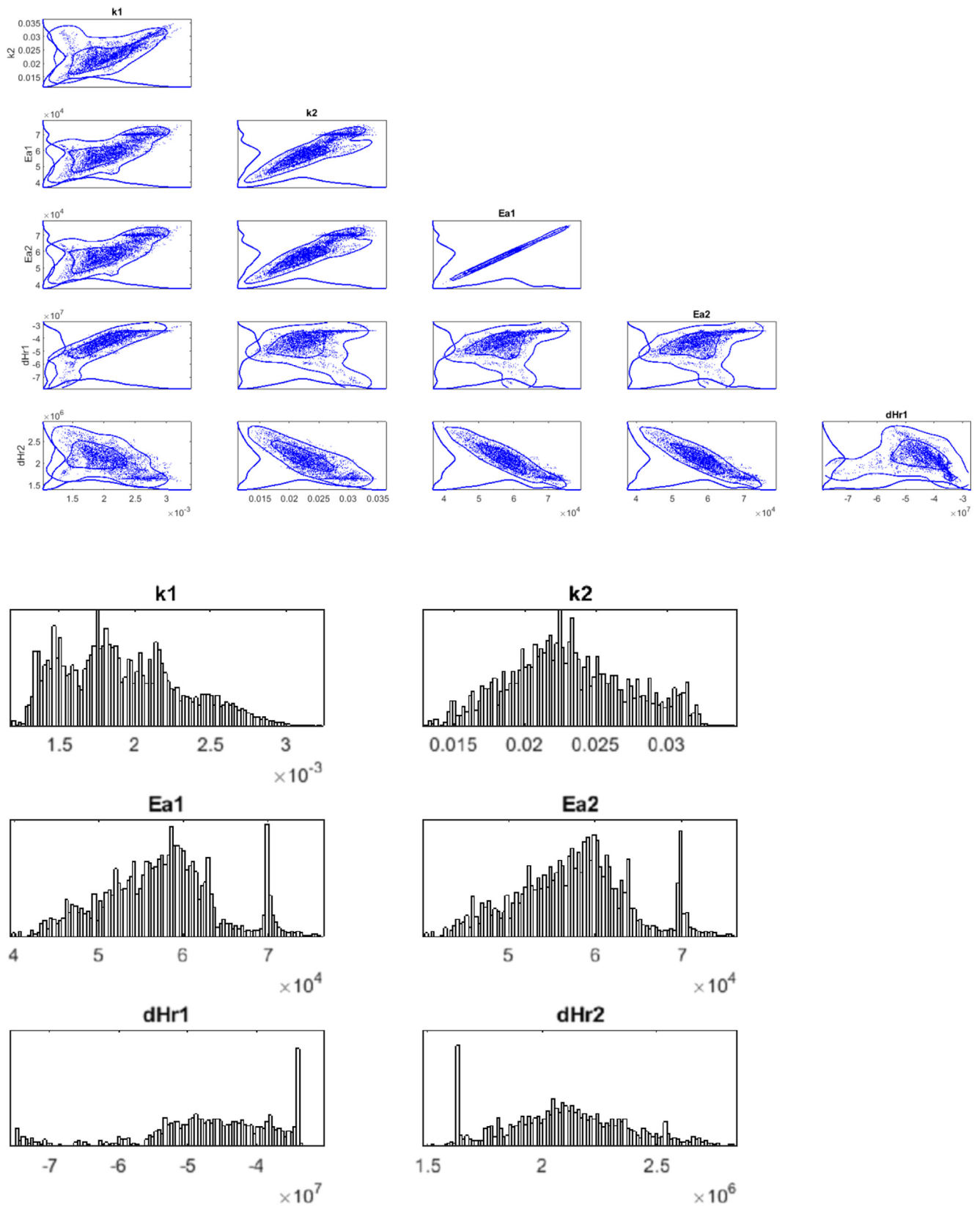


Fig. 6. MCMC analysis of the parameters in the improved model. Mutual correlations of the parameters (upper) and probability distributions of the parameters.



#### 4. Conclusions

The use of simple adiabatic CSTRs for the determination of the kinetics of homogeneous liquid-phase reactions was illustrated. The theoretical basis of the method was described and the strongly exothermic reaction between sodium thiosulphate and hydrogen peroxide was used as a model system to illustrate the concept. The proposed approach enables a very rapid determination of the reaction kinetics for relatively simple systems, because it is based on temperature measurements only. A large temperature spectrum can be screened by a single experiment. In case of complex kinetics for multireaction systems, it is necessary to combine the temperature measurements with on line or off line chemical analysis of the participating components. The technology could be refined further by decreasing the size of the CSTR and coupling several small CSTRs in parallel. In this way, several inlet or initial temperatures and reactant mole ratios could be screened rapidly and simultaneously.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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