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Thermochimica Acta 310 (1998) 173–178

thermochimica acta

Communication between calorimetric experiment and continuous data evaluation during the incomplete reaction run[1]

A. Kemmler*, H.L. Anderson, D. Haberland, K. Heldt, R. Strey

University of Greifswald, Institute of Physical Chemistry, Soldtmannstr. 23, D 17489 Greifswald, Germany

Received 30 April 1997; received in revised form 4 July 1997; accepted 4 July 1997

Abstract

The kinetic control of exothermic reactions plays an important role in chemical safety technology. Predictions of thermal explosions by runaway, e.g. redox reactions, poly reactions, and decompositions, are required in case of simple as well as of complex reactions. Activation parameters of chemical reactions are often stressed by systematic errors which are caused by failures in accuracy of measurement and calibration. The influence of systematic errors for some selected reactions has been investigated by the software package TA-kin. The coupling between continuous data evaluation software and the precision calorimeter ACTRON 5.0, including a safety scenario equipment, was established to test the validity of calculated runaway predictions under practical conditions. Measured data are applied for kinetic evaluations by nonlinear optimization methods in real time. In this way, the experimental investigations of reaction systems become possible beyond the *point of no return* without any danger for the laboratory. © 1998 Elsevier Science B.V.

Keywords: Calorimetry; Kinetic; Safety; Software

1. Introduction

The occurrence of undesired secondary reactions, e.g. diazotizations or nitrations [1–3], in chemical processes is mostly accompanied by an increasing risk potential. Kinetic evaluations during the incomplete reaction can be performed to predict a thermal explosion.

Generally, uncertainties of temperature signals have to be taken into account. Furthermore, reactor functions such as the heat-exchange coefficient, $K(T,v)$, and the heat capacity of the loaded reactor, $C_p(T,v)$, could contain systematic errors due to nonadequate calibration.

The influence of systematic errors for some selected reactions has been investigated by the software package TA-kin [4]. Especially in the case of an unwanted autocatalysis, the process becomes increasingly dangerous, as has been shown by a lot of computer experiments. Hence, the question of a safe prediction of the runaway case is closely connected with the actual error standard in the laboratory.

2. Early recognition of thermal explosion

Exothermic reactions of rather high activation energies may tend to cause a runaway as shown in Fig. 1. This thermal risk can be characterized by the time

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*Corresponding author. Fax: 00 49 3834-038356295; e-mail: kemmler@gryps1.rz.uni-greifswald.de

[1] Presented at the Twelfth Ulm-Freiberg Conference, Freiberg, Germany, 19–21 March 1997

PII S0040-6031(97)00393-6

taken to reach maximum rate $\mathrm{TMR}_{\mathrm{ad}}$ under adiabatic conditions and the adiabatic temperature rise ΔT_{ad} [5]. According to these values, characterizing the worst case, someone may derive criteria for on-line process monitoring [6]:

- critical temperature, T
- critical self heating rate, $\mathrm{d}T/\mathrm{d}t$
- critical heat balance, $\mathrm{d}q/\mathrm{d}t$
- critical progressive derivatives of temperature, $\mathrm{d}^2T/\mathrm{d}t^2$.

The application of numerical methods is advisable to obtain these values from the experimental run. Smoothing procedures and nonlinear regression methods based on simple explicit functions are in common use. Certainly, they do not allow to obtain any reliable prediction about the further temperature course. For that purpose higher level methods have to be taken into account, e.g. model classification by parameter estimation or application of neuronal networks. In practice, thermal explosion occurs after passing a relative long induction time. Evaluation within this range based on kinetic models is our aim to predict a critical situation.

3. Data exchange during the experimental run

On-line evaluation requires the coupling of experimental equipment and personal computer. The communication between the precision calorimeter ACTRON 5.0 [7] and an IBM compatible PC shows Fig. 2.

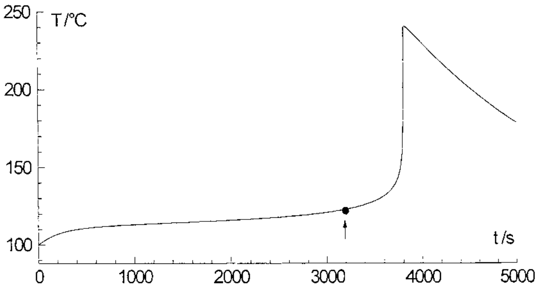

Fig. 1. Thermal explosion during a batch run due to undesired consecutive reaction with high activation energy and exothermic enthalpy. At the marked point, the reaction heat release rate reaches the cooling capacity, so that the system becomes critical. A+B→C: $\ln k_0=20$, $E_A=80$ kJ/mol, $\Delta H=-40$ kJ/mol; and C→D: $\ln k_0=40$, $E_A=160$ kJ/mol, $\Delta H=-400$ kJ/mol. Note that the initial temperature (100°C) is a prerequisite for the runaway. At lower initial temperatures (for instance 90°C) the reaction system behaves normally.

The ACTRON software records measured data and passes them to the evaluation software TA-kin by *Dynamic Data Exchange*. This enables the kinetic evaluations of the temporary data according to a set of assumed models of chemical mechanisms. The evaluation is performed by nonlinear regression with numerical integration of the rate equations and the heat-balance equation. If a critical situation is predicted, the software will activate special emergency functions of the calorimeter which include the addition of an inhibitor or the start of safety pumps. The very fast safety pumps represent the main components of the safety scenario equipment. They work simultaneously, one empties the reactor while the other purges it with cold solvent. In this way, kinetic evaluations become possible even under conditions that characterize a case of runaway.

4. Modelling of chemical reactions

The mathematical treatment of kinetics is based on the general kinetic rate law and the heat-balance equation according to Tian. Up to now, a complete analytical solution of the differential equation system (1a)–(1c) is not possible, therefore we perform numerical integrations by the very robust Runge–Kutta methods using adaptive step control. It proves to be a comfortable choice to do this job [8].

$$\dot{\xi}_j = v k_j(T_{\mathrm{R}}) \prod_{i=1}^{M} c_i^{n_{j,i}} \tag{1a}$$

$$\text{with } c_i = \frac{1}{v}\left(n_{i,0} + n_{i,\mathrm{add}} + \sum_{j=1}^{R} \nu_{j,i}\xi_j\right)$$

$$k_j(T_{\mathrm{R}}) = \exp\left(\ln k_{0,j} - \frac{E_{\mathrm{A},j}}{RT_{\mathrm{R}}}\right)$$

$$\dot{T}_{\mathrm{R}} = -\frac{\sum_{j=1}^{R} \Delta H_j \dot{\xi}_j + K(T_{\mathrm{R}} - T_{\mathrm{U}}) + k\dot{v}(T_{\mathrm{R}} - T_{\mathrm{U}})}{C_{\mathrm{p,R}} + kv + \sum_{j=1}^{R} \Delta C_{\mathrm{p},j}\xi_j} \tag{1b}$$

$$\dot{T}_{\mathrm{S}} = \frac{1}{\tau_{\mathrm{S}}}(T_{\mathrm{R}} - T_{\mathrm{S}}) \tag{1c}$$

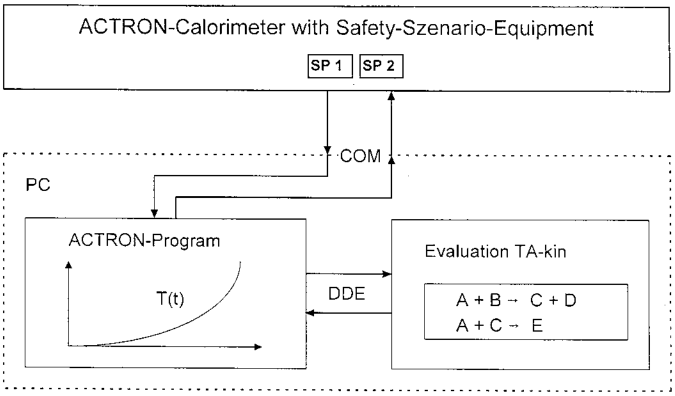

Fig. 2. Communication between calorimeter ACTRON and computer by serial interface COM and *Dynamic Data Exchange*.

Reaction kinetics is expressed by rate laws, $d\xi/dt$, containing the activation parameters for each partial reaction, Eq. (1a). The dividend in the dT_R/dt of Eq. (1b) consists of a chemical heat release term, a heat-exchange term and a heat-input term due to adding components with the flow rate dv/dt. Thermal inertia of the temperature sensor, see Eq. (1c), can be characterized by a time constant τ_S.

Table 1
Considered experimental errors

Accidental errors	Systematic errors
Normal distributed scatter	Uncertainties of calibration coefficients
σ=50–200 mK	$\Delta K/K$=−50–100% $\Delta C_p/C_p$=−50–100% Temperature shift ΔT=1000 mK

5. Kinetic evaluation during induction periods

The embedding of a numerical integration procedure in a nonlinear least-squares method by Marquardt and Levenberg [9] leads to an iterative parameter optimization tool for ordinary differential equations. Primary measured temperature data as well as concentrations, etc. can be included in the evaluation procedure implemented into TA-kin. With respect to accidental and systematic errors, which principally influence the measurement, we considered several types of experimental errors listed in Table 1.

Performing a parameter estimation using error burdened data within the induction period results in shifted activation parameters, see Table 2. But what follows for the prediction of TMR? The examples in Fig. 3 show the prognosis for the consecutive reaction system of Fig. 1. In each case, the threatening runaway is predicted although the activation parameters were changed up to 10% by the kinetic evaluation. It is caused by the correlation between activation parameters in the Arrhenius equation. The mathematical structure produces the so-called 'compensation effect', which results similar simulations for a surprising wide range of E_A−ln k_0 sets [4]. Of course, this is a handicap for each operator who wants to determine the 'real' activation values. But for the prediction of possible runaways this effect should be less important.

Autocatalytic reactions with high enthalpies are often of extreme thermal risk. However, the induction period contains the information that a thermal explosion will occur. Fig. 4 shows the calorimetric course of an autocatalytic batch reaction according to Table 3 with a maximum temperature jump to 189°C after 22921 s.

From the simulated curve between 0 and 21500 s, exactly 122 data points were burdened with normal distributed errors. Afterwards, these data were used for the estimation of three activation parameters. Next,

Table 2
Results of kinetic evaluations, SD=200 mK, see also Fig. 3

Error type	Reaction	ln k_0 [a]	E_A (kJ mol^{-1})	t_{max} (s)	T_{max} (°C)
None	A+B→C	20	80	3805	240
	C→D	80	160		
SD [b]	A+B→C	21.6	84.9	3807	241
	C→D	40.29	160.9		
$\Delta K/K$ and SD	A+B→C	25.0	95.6	3804	234
	C→D	38.83	155.7		
ΔT and SD	A+B→C	18.5	76.4	3800	251
	C→D	42.89	169.6		

[a] Dimension of k_0 is [s^{-1}(mol/l)$^{1-n}$], n=2 for A+B→C, n=1 for C→D.
[b] SD=200 mK.

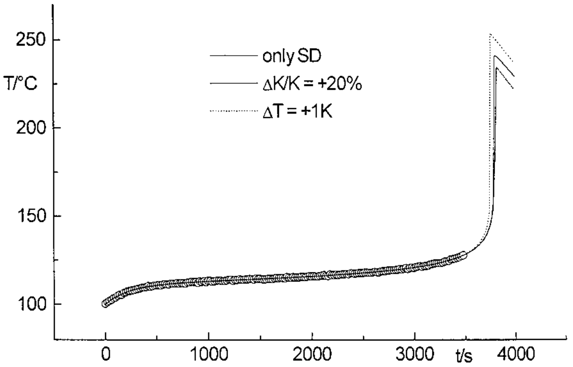

Fig. 3. Runaway predictions from kinetic evaluations of the range 0–3500 s. For original data see Fig. 1, for estimated parameters see Table 2.

Table 3
Kinetic model for an autocatalytic reaction

	A→B	A+B→2B
ln k_0 [a]	20	18
E_A (k Jmol^{-1})	85	65
ΔH (kJ mol^{-1})	−500	−500
$n(A)$	1	1
$n(B)$	0	1

[a] Dimension of k_0 is [s^{-1}(mol/l)$^{1-n}$], n=2 for A+B→2B, n=1 for A→B.

a forward simulation predicts a thermal explosion with a maximum temperature jump to 189°C after 22949 s.

However, systematic errors in the reactor model have to be taken into account. Different types of false reactor constants have been implemented. Fig. 5 illus-

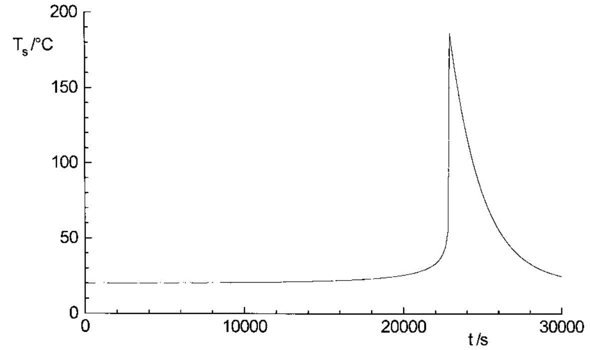

Fig. 4. Autocatalytic reaction in an isoperibolic reactor, see also Table 3. C_p=2500 J K^{-1}, K=1.25 J K^{-1} s^{-1}, v=1 l, [A]$_0$=1 mol l^{-1}, [B]$_0$=0.

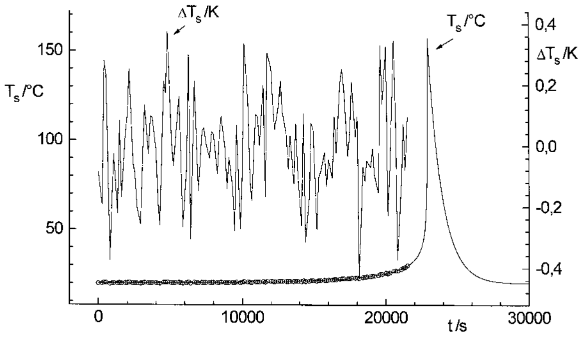

Fig. 5. Kinetic evaluation of false data (○, σ=200 mK and systematic error in heat-exchange coefficient of 100%) and forward simulation (———). $\Delta T(t)$ represents the difference between false data and simulation curve.

trates the results of an optimization assuming too large heat exchange, then the prediction shows a maximum temperature jump to 158°C after 22896 s. Note that the curve of residues ΔT does not allow to verify a systematic error in the model.

6. Conclusions

Continuous control of reaction systems requires comprehensive knowledge of the reaction chemistry as well as higher level mathematical operations to obtain reliable predictions about the further run. High-precision calorimetry, as realized by the ACTRON series, enables detailed kinetic investigations to obtain necessary information about the reaction behaviour in a wide range of external conditions that may cause critical situations. The well-known numerical procedures of TA-kin for Windows can be applied successfully using PCs to perform complex computations at small time expense.

Considering data as well as reactor model uncertainties in practice, the on-line reaction control by kinetic evaluation should be a good tool for safer prediction of critical situations. In this way, process risk in lab and plant decreases because the accident probability diminishes by a reliable, early forecast of a runaway.

Symbol	Name	Context	Unit
t	time		s
ξ	amount of conversion	$d\xi = dn_i/\nu_i$	mol
ν	stoichiometric coefficient		
c	concentration		$\mathrm{mol\ l^{-1}}$
k_0	frequency factor		$\mathrm{(mol\ l^{-1})^{1-n}\ s^{-1}}$
E_A	activation energy		$\mathrm{kJ\ mol^{-1}}$
ΔH	reaction enthalpy		$\mathrm{kJ\ mol^{-1}}$
ΔC_p	reaction heat capacity		$\mathrm{J\ mol^{-1}\ K^{-1}}$
n	amount of substance		mol
n	(partial) reaction order		
R	gas constant	$R=8.31441\mathrm{E}{-3}$	$\mathrm{kJ\ mol^{-1}\ K^{-1}}$
R	count of chemical reactions		
M	count of reaction components		
v	filled reactor volume		l
$C_{p,R}$	reactor heat capacity		$\mathrm{J\ K^{-1}}$
k	reaction rate constant	$k=k_0 \exp(-E_A/RT)$	$\mathrm{(mol\ l^{-1})^{1-n}\ s^{-1}}$
k	linear coefficient of reactor volume dependent heat capacity	$k=(C_p-C_{p,R})/v$	$\mathrm{J\ K^{-1}\ l^{-1}}$
K	heat-exchange coefficient		$\mathrm{J\ K^{-1}\ s^{-1}}$
τ_S	sensor time constant		s
τ_R	reactor time constant	$\tau_R=C_p/K$	s
T_S	sensor temperature		°C
T_R	reactor temperature		°C
T_U	cooling temperature		°C
ΔT	residue (of temperature)		K
σ, SD	standard deviation (of temperature)		K
TMR	time to maximum rate		s

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