*Journal of Thermal Analysis, Vol. 38 (1992) 2729-2747*

# CHARACTERISATION OF AN EXOTHERMIC REACTION USING ADIABATIC AND ISOTHERMAL CALORIMETRY

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A simple esterification reaction is used to demonstrate standard procedures for determining the thermokinetic parameters of an exothermic reaction from adiabatic calorimetric data. The influence of variations in the heat capacity of the sample due to changes in temperature and concentration is explored. Shortcomings in the simple interpretation of adiabatic data are identified and isothermal heatflow calorimetry is used to reveal autocatalytic effects which were not apparent from the adiabatic experiments. A more rigourous interpretation of the adiabatic and isothermal data is outlined and used to predict the conditions which can lead to exothermic runaway in a batch reactor. Mathematical simulation of the conditions in a jacketed reactor is used to demonstrate the importance of developing reliable kinetic expressions before assessing the safety of a batch process.

**Keywords:** adiabatic and isothermal calorimetry, batch reactor, esterification kinetics, mathematical simulation

## 1. Introduction

In order to evaluate the hazards associated with exothermic reaction or decomposition, it is necessary to determine the temperature and concentration dependence of the rate of heat generation. Adiabatic techniques such as accelerating rate calorimetry [1], adiabatic dewar calorimetry [2] and, more recently, adiabatic calorimetry for the design of emergency pressure relief systems [3, 4], are used extensively to determine the thermokinetic properties of an exothermic reaction. The broad objective of these techniques is to determine the rate of temperature (and pressure) rise as a function of temperature for an exothermic reaction under conditions where heat losses to the surroundings are eliminated. A number of important assumptions are made in order to derive the thermokinetic parameters of an exothermic reaction from experimental data on the rate of self-heating under adiabatic conditions:

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– the reaction mechanism is assumed to be independent of temperature so that the temperature and concentration dependencies can be treated separately.

– the total heat generated is evaluated directly from the adiabatic temperature rise assuming constant heat capacity.

– at any stage in the reaction, the heat generated is assumed to correspond to changes in concentration such that the rate of change of concentration and the rate of heat generation are directly proportional to the rate of temperature rise under adiabatic conditions, with the extent of reaction equal to the temperature increase expressed as a fraction of the total adiabatic temperature rise.

– the temperature dependence of the reaction rate constant is assumed to follow the Arrhenius equation.

– the dependence of reaction rate on concentration is represented by a single order of reaction with fractional values used so that complex mechanisms can be represented by simple overall kinetic expressions.

These assumptions are necessary particularly where only limited data are available on physical and chemical properties of the reaction system. However, simple interpretations based on these assumptions can lead to major innaccuracies in determining safe process conditions, and temperature evolutions during industrial production.

The form of the experimental record of self-heat rate against time for an exothermic reaction proceeding under adiabatic conditions tends to be dominated by the temperature, rather than the concentration, dependence of reaction rate. Adiabatic experiments can fail to detect concentration effects such as autocatalysis which become important when the reaction is performed under industrial conditions.

The present study was designed to illustrate the problems which can arise if hazard evaluation is based on a single adiabatic technique without proper reference to the process chemistry and without investigating the reaction under isothermal conditions.

Adiabatic calorimetry has been applied to an exothermic reaction, and the results are interpreted, initially, on the assumption that no other information is available on the reaction mechanism or the variation of the rate of heat generation with time under isothermal conditions. Thermokinetic parameters are derived assuming a constant heat capacity for the reaction system. The known chemistry and stoichiometry of the reaction system are then used to determine the changes in heat capacity during the course of reaction and the effect of these variations on the evaluated thermokinetic parameters is explored.

The results of isothermal heat flow calorimetry are used to identify the shortcomings of the simple interpretation. A revised rate equation is proposed to take account of both the adiabatic and isothermal data and corresponding values for the thermokinetic constants are evaluated.

The simple interpretation of adiabatic data, including the variations in heat capacity, is used to predict temperature-time histories when the reaction is performed in a jacketed reactor with well established heat transfer characteristics. The predictions are compared with an experimental investigation of the reaction in a small jacketed reactor under conditions which result in exothermic runaway. A second set of simulated temperature-time histories are produced based on the revised interpretation of the calorimetric data taking into account isothermal results. The revised model is shown to produce much improved agreement between theory and experiment and a more reliable approach to hazard evaluation.

## 2. Experimental procedure

### 2.1 *Reaction system*

The esterification reaction between sec.butyl alcohol and propionic anhydride was chosen for this investigation,

| | | | | | | |
|---|---|---|---|---|---|---|
| $C_2H_3CH_2CHOHCH_3$ | + | $(CH_3CH_2CO)_2O$ | → | $C_2H_5CO_2(CH_3)CHC_2H_5$ | + | $C_2H_5CO_2H$ |
| sec. butyl<br>alcohol | | propionic<br>anhydride | | sec. butyl<br>propionate | | propionic<br>acid |

The reaction is moderately exothermic and can be catalysed by the addition of small quantities of concentrated sulphuric acid. Acidified butanol was prepared separately, and them mixed with propionic anhydride in the calometers. Calorimetric data are presented for reaction mixtures containing 0.8% sulphuric acid ( expressed as a percentage of the weight of butylalcohol). This composition produced rates of heat generation which could be measured within the specifications of the calorimeters and, under isoperibolic conditions, produced critical phenomena (runaway reactions) over an experimentally accesible temperature range.

### 2.2 *Adiabatic calorimetry*

The temperature dependence of the rate of self-heating under adiabatic conditions was determined using the PHI-TEC calorimeter [4], shown schematically in Fig. 1. The operation of this device is similar to the accelerating rate calorimeter, ARC [1] and the vent sizing package VSP [3]. The sample is held in a stainless steel container provided with a magnetic stirrer and with thin walls in order that the experimental results are not strongly influenced by the heat capacity of the container. Adiabatic conditions are maintained by using electrical heaters to match the temperature of the surroundings to that of the sample. A separate heater is used to raise the temperature of the sample to the selected initial temperature and then adiabatic conditions are maintained as the temperature and pressure increases due to exothermic reaction of the sample. If there is no increase in temperature due to exothermic reaction, the instrument can operate in 'heat-wait-search' mode by using the sample heater to produce a series of temperature steps until exothermic reaction is detected. Rupture of the thin-walled sample container is prevented by automatically applying nitrogen pressure to the outside of the container to compensate for internal pressure generated due to exothermic reaction.

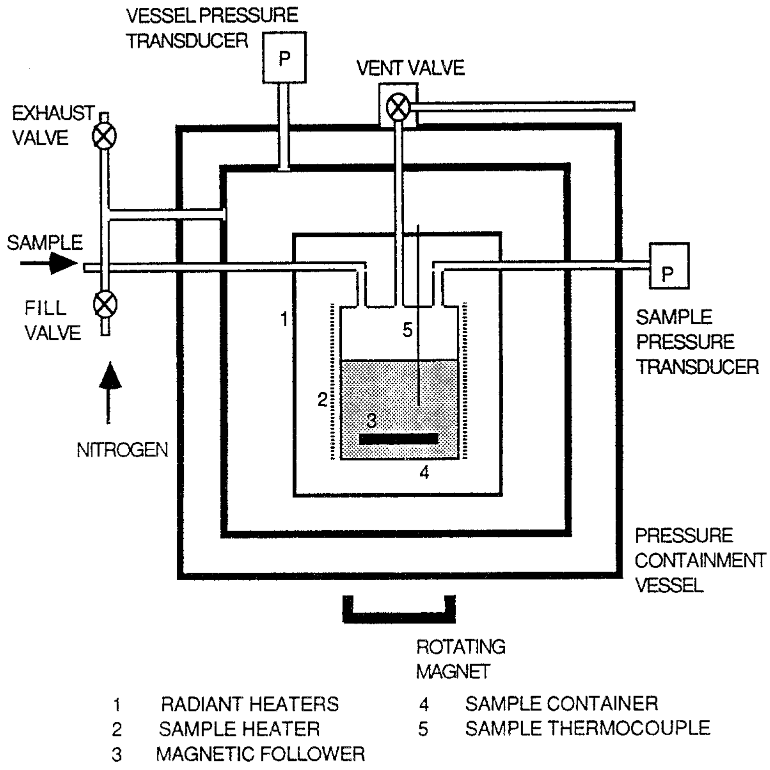

**Fig. 1** Schematic diagram of PHI-TEC adiabatic calorimeter

A series of measurements were made using equimolar mixtures of sec.butyl alcohol and propionic anhydride catalysed by various concentrations of sulphuric acid with a total sample mass of 60 g. Reagents were added with the sample container positioned inside the calorimeter and adiabatic conditions were established from ambient temperature without using the 'heat-wait-search' mode of operation.

Figure 2 shows the plot of self-heat rate against temperature for the esterification reaction catalysed by the addition of 0.8% sulphuric acid (expressed as a percentage of the mass of butyl alcohol). Similar results were obtained at other acid concentrations with increases in sulphuric acid concentration causing a progressive increase in the rates of self-heating. Self-heat rateswere calculated from the temparature-time data using software provided by the instrument manufacturer.

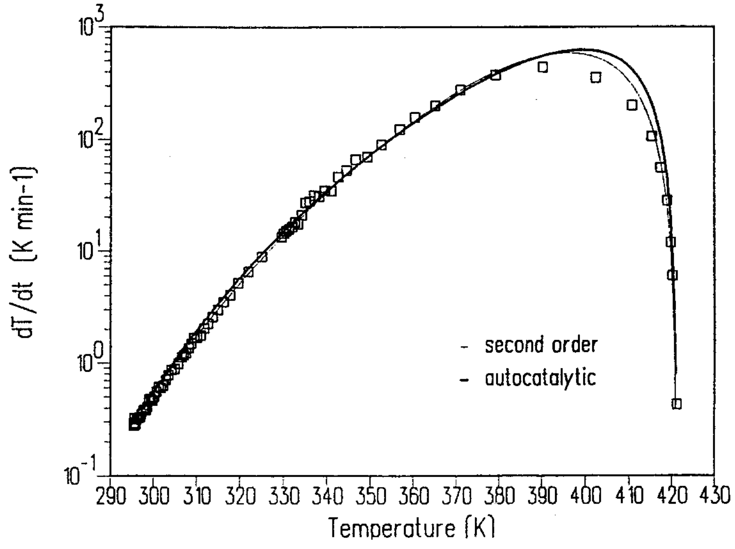

**Fig. 2** PHI-TEC plots of the rate of self-heating for the esterification reaction catalysed by the addition of 0.8% $H_2SO_4$. (See text for significance of fitted curves)

### *2.3 Isothermal heat-flow calorimetry*

The isothermal variation of the rate of heat generation with time was measured using the Mettler RC1 reaction calorimeter [5], shown schematically in Fig. 3. This instrument comprises a computer controlled jacketed reactor (2 litre capacity) provided with an agitator, condenser and feed system. The heat-transfer fluid circulating through the reactor jacket can be maintained at a constant temperature or the jacket temperature can be controlled so as to maintain the reactor contents at a constant temperature.

At constant reactor temperature, the rate of heat generation due to exothermic reaction is equal to the rate of heat flow between the reactor and the jacket and is given by:

$$q_g = U \cdot S \cdot (T_r - T_j) \tag{1}$$

The heat transfer coefficient $U$ was determined by calibration using an electrical immersion heater.

Isothermal measurements of the rate of heat generation were made for the esterification reaction catalysed by 0.8% sulphuric acid. Equimolar mixtures were used with a total sample mass of 1.36 kg. The acidified alcohol was added to the reactor and time was allowed for the control system to achieve the temperature selected for isothermal measurement. Propionic anhydride at ambient temperature was then added quickly to the reactor and the reaction was allowed to proceed until the jacket temperature became equal to the reactor temperature, indicating that the reaction was complete.

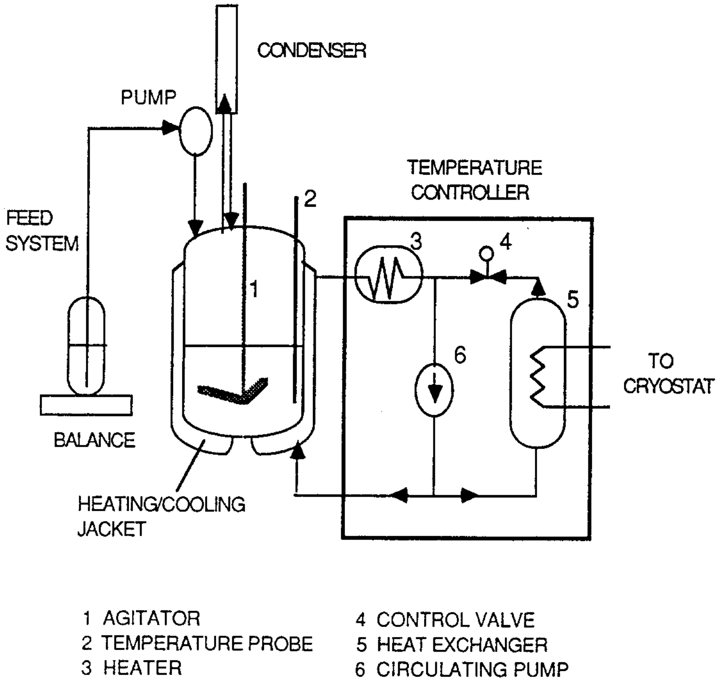

**Fig. 3** Schematic diagram of RC1 reaction calorimeter

Figure 4 shows the variation of jacket temperature and reactor temperature with time for the esterification reaction with a reactor temperature set point of 303.5 K. Small increases in $T_r$ occur at high rates of heat generation, when the difference between $T_r$ and $T_j$ is large. This is due to the operation of the control system and depends on the values selected for the proportionality constant.

Measurements made at a lower set point (295.6 K) produced a temperature-time profile similar to Fig. 4 but led to no significant changes in the interpretation (and evaluated parameters) as outlined in the following discussion. At a higher set point (313.5 K) large rates of heat generation caused an uncontrolled increase in the reactor temperature and the automatic application of full cooling to the reactor jacket.

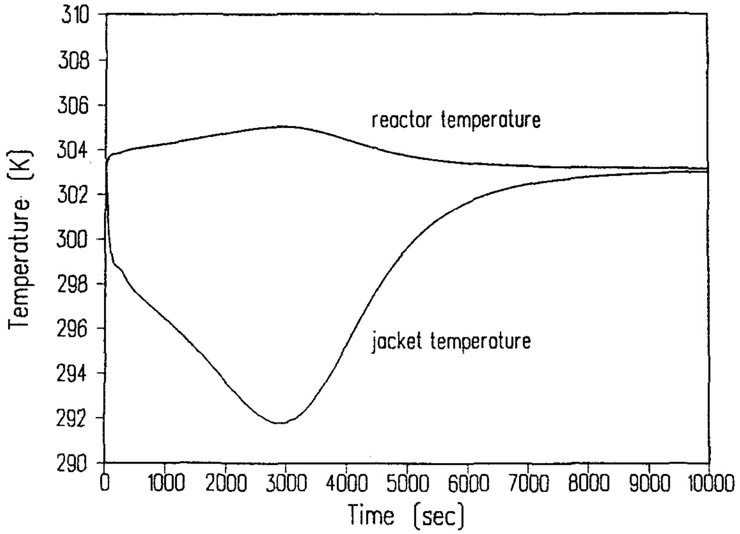

**Fig. 4** Variation of reactor temperature and jacket temperature during batch esterification reaction (catalysed by 0.8% $H_2SO_4$) in RC1 reaction calorimeter operating in $T_r$ mode (set point 303 K)

### 2.4 *Investigation of critical conditions in a laboratory-scale reactor*

The critical conditions which could lead to exothermic runaway were determined for the esterification reaction in the 2 litre reactor by configuring the RC1 reaction calorimeter [5] to operate at constant jacket temperature (without exploiting the heat-flow calorimetric capabilities of the instrument). Experiments were performed at a series of fixed jacket temperatures for the esterification reaction catalysed by the addition of 0.8% sulphuric acid. Equimolar mixtures were used with a total sample mass of 1.36 kg. The acidified *sec*-butyl alcohol was added to the reactor and allowed to reach thermal equilibrium with the reactor jacket before the rapid addition of propionic anhydride which had been preheated to the same temperature as the reactor jacket.

Figure 5 shows the variation of reactor temperature with time for experiments at a series of jacket temperatures ranging from 293.9 to 308.2 K. The drop in temperature at the start of each experiment is due to endothermic mixing of reagents. At the conclusion of each experiment samples were taken and chemical analysis showed that the reaction had gone to completion.

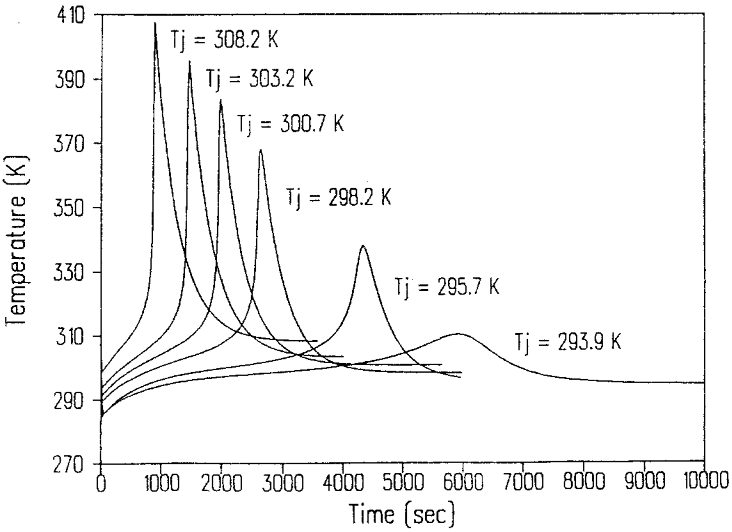

**Fig. 5** Variation of reactor temperature during esterification reaction (catalysed by 0.8% $H_2SO_4$) in the RC1 reaction calorimeter at a series of fixed jacket temperatures

## 3. Characterisation of a simple exothermic reaction from calorimetric data

In order to determine the thermokinetic parameters of an exothermic reaction from calorimetric data it is necessary to adopt a simplified representation of the temperature and concentration dependencies. If a simple nth order reaction is assumed, the rate equation can be written in the form:

$$\frac{dx}{dt} = k_T \cdot (1-x)^n \tag{2}$$

The temperature dependence of the rate constant, $k_T$, is usually assumed to follow the Arrhenius equation:

$$k_T = A \cdot \exp(-E / RT) \tag{3}$$

If the enthalpy change is proportional to the change in conversion, the rate of heat generation due to a simple exothermic reaction is given by:

$$q_g = -\Delta H \cdot m_s \cdot (1-x)^n \cdot A \cdot \exp(-E / RT) \tag{4}$$

and the corresponding rate of self-heating of a sample in a thermally isolated container is:

$$\frac{dT}{dt}=\frac{\Delta H\cdot A\cdot(1-x)^n}{C_p\cdot\Phi}\cdot\exp(-E/RT) \tag{5}$$

where the thermal dilution factor, $\Phi = (m_s\cdot C_p + m_c\cdot C_{pc})/m_s\cdot C_p$, takes account of the distribution of heat between the sample and the sample container.

Standard procedures for determining the exothermicity ($\Delta H$) and the kinetic constants ($A$, $n$ and $E$) from adiabatic self-heat rate data (assuming $C_p$ constant) are described in the following section. The effect of including the temperature and concentration dependence of $C_p$ is then explored. Finally, the use of isothermal heat-flow calorimetry to determine the exothermicity and concentration dependence is described.

### *3.1 Adiabatic data assuming constant $C_p$*

#### 3.1.1 Exothermicity

If $C_p$ is assumed constant, $\Delta H$, can be evaluated directly from the adiabatic data using the expression:

$$\Delta H=-\Delta T_{ad}\cdot C_p\cdot\Phi \tag{6a}$$

The value of $\Delta H$ for the esterification reaction, calculated using Eq. (6a), is given in Table 1.

#### 3.1.2 Kinetic constants

Under adiabatic conditions at constant $C_p$, temperature changes are directly proportional to changes in concentration and the extent of reaction is given by:

$$x=\frac{T-T_i}{\Delta T_{ad}}=1-\frac{T_f-T}{\Delta T_{ad}} \tag{7a}$$

From Eqs (5, 6a and 7a)

$$\frac{dx}{dt}=\frac{1}{\Delta T_{ad}}\frac{dT}{dt}=\frac{(T_f-T)^n\cdot A}{\Delta T_{ad}^n}\exp(-E/RT) \tag{8a}$$

Thus a plot of $\ln(dx/dt\cdot(1/1-x)^n)$ or $\ln(dT/dt\cdot(1/(T-T_f)^n)$ against $1/T$ gives a straight line if the correct value of $n$ is chosen, and $A$ and $E$ can be evaluated from the intercept and the gradient respectively.

Application of this procedure to the self-heat rate data for the esterification reaction (Fig. 2) gave the plots shown in Fig. 6. It can be seen that good linear correlation with the experimental data is obtained when second order reaction kinetics ($n$ = 2) are assumed. The corresponding values for $A$ and $E$ are listed in Table 1 (column 1). The temperature dependence of $(dT/dt)_{ad}$, calculated using these parameters, is plotted against temperature in Fig. 2 for comparison with the experimentally determined values. Reasonable agreement can be seen between the fitted curve and experimental data.

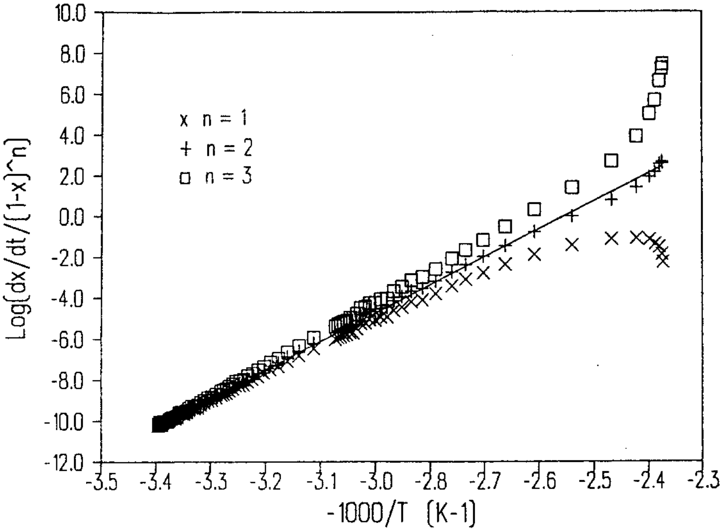

**Fig. 6** Determination of order of reaction, *n*, from adiabatic data (PHI-TEC) for esterification reaction (catalysed by 0.8% $H_2SO_4$)

### *3.2 Adiabatic data including variation of $C_p$*

#### 3.2.1 Exothermicity

Substantial variations of $C_p$ with temperature and composition imply that the heat of reaction will show significant temperature dependence.

Under adiabatic conditions, the heat released due to exothermic reaction (at $T_i$) raises the temperature of the products and container to the final temperature, and, if the heat capacity of the sample container ($C_{pc}$) is assumed constant, Eq. (6*a*) becomes:

$$\Delta H_{Ti} = -\int_{T_i}^{T_f} C_{pp}\cdot dT - \frac{m_c\cdot C_{pc}\cdot \Delta T_{ad}}{m_s} \qquad (6b)$$

$\Delta H_{Ti}$ for the esterification reaction, calculated using Eq. (6b) and published data [6] for the temperature dependence of the heat capacity for the reaction products ($C_{pp}$), is given in Table 1 (column 2).

The temperature dependence of $\Delta H$ can be evaluated using Kirchoff's equation:

$$\Delta H_{\mathrm{T}} = \Delta H_{\mathrm{Ti}} + \int_{T_i}^{T} (C_{\mathrm{pp}} - C_{\mathrm{pr}}) \cdot \mathrm{d}T \tag{9}$$

$\Delta H_{\mathrm{Tf}}$ for the esterification reaction, calculated using Eq. (9), is given in Table 1.

Table 1 shows that inclusion of the temperature and concentration dependences of $C_{\mathrm{p}}$ leads to significant differences in the evaluated heat of reaction.

**Table 1** Thermokinetic parameters for the esterification reaction (catalysed by 0.8% $H_2SO_4$) derived from adiabatic data (PHI-TEC). ($T_i$ = 295 K, $T_f$ = 421 K)

| | Normal kinetics $C_{\mathrm{p}}$ constant | Normal kinetics $C_{\mathrm{p}}$ variable | Autocatalytic kinetics $C_{\mathrm{p}}$ variable |
|---|---|---|---|
| rate equ. | $\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{T}} \cdot (1-x)^n$ | $\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{T}} \cdot (1-x)^n$ | $\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{T}} \cdot (1-x)^n \left( \frac{x}{B-\sqrt{x}} + C \right)$ |
| $\Delta H_{\mathrm{Ti}}$/ kJ·kg$^{-1}$ | 295 | 309 | 309 |
| $\Delta H_{\mathrm{Tf}}$/ kJ·kg$^{-1}$ | 295 | 339 | 339 |
| $n$ | 2 | 2 | 2 |
| $E$/ kJ·mol$^{-1}$ | 104.5 | 105.5 | 69.21 |
| ln ($A$) | 32.39 | 32.54 | 20.07 |
| $B$ | – | – | 1.051 |
| $C$ | – | – | 0.118 |

### 3.2.2 Kinetic constants

The enthalpy change in going from reactants at $T_i$ to reactants and products at $T$ is independent of path such that, for an adiabatic system, the heat required to raise the temperature of the reactants and sample container from $T_i$ to $T$ is balanced by the heat generated by reaction at $T$, and the conversion at $T$ is given by:

$$x_T = \frac{1}{\Delta H_T}\int_{T_i}^{T} C_{pr}\cdot dT + \frac{m_c\cdot C_{pc}\cdot (T-T_i)}{m_s\cdot \Delta H_T} \tag{7b}$$

and the rate of conversion is given directly by:

$$\frac{dx}{dt} = -\frac{U\cdot S\cdot (T_r-T_j)}{m_s\cdot \Delta H} \tag{8c}$$

Figure 7 shows the plot of rate against conversion determined from the isothermal heat flow calorimetric data for the esterification reaction (Fig. 5). The second order dependence of d$x$/d$t$ on $x$ (predicted by the simple interpretation of adiabatic data) is also plotted in Fig. 7 for comparison.

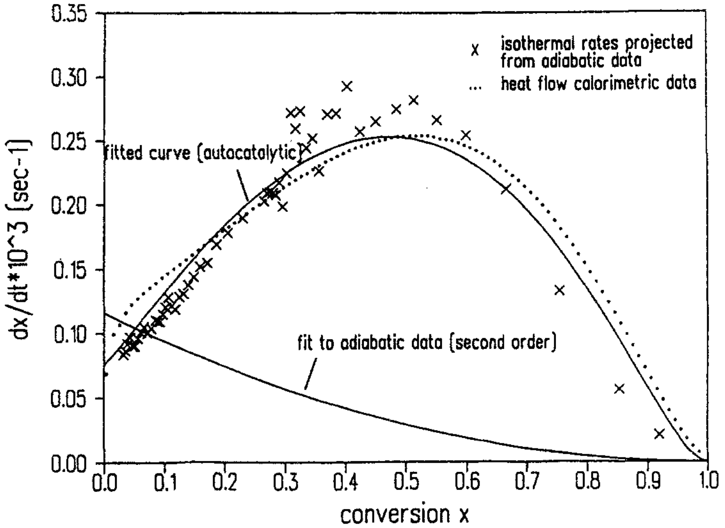

**Fig. 7** Isothermal variation of rate with conversion for esterification reaction (see text for significance of fitted curves and extrapolated adiabatic data)

It is clear from Figs 5 and 7 that simple *n*th order kinetics cannot describe satisfactorily the temporal evolution of the rate of heat generation at constant temperature. It is evident from the initial increase in the difference between $T_r$ and $T_j$ that the process is autocatalytic. Autocatalysis can be expected since the catalytic effect due to the sulphuric acid would be augmented by the increase in acidity due to the formation of propionic acid. An increase in acidity may also result from increased dissociation of the sulphuric acid as the composition of the reacting medium changes.

The rate of conversion at $T$ is related to the rate of temperature rise by the expression:

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{m_s\cdot((1-x)\cdot C_{\mathrm{pr}}+x\cdot C_{\mathrm{pp}})+m_c\cdot C_{\mathrm{pc}}}{\Delta H_{\mathrm{T}}}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{8b}$$

Equations 7b and 8b have been used to determine values of $x_{\mathrm{T}}$ and $(\mathrm{d}x/\mathrm{d}t)_{\mathrm{T}}$ from the adiabatic self-heat rate data for the esterification reaction. The plots of $\log(\mathrm{d}x/\mathrm{d}t/(1-x)^n)$ (Fig. 6) are indistinguishable from those derived assuming constant $C_{\mathrm{P}}$. Good correlation with the experimental data was again obtained for $n = 2$. Linear regression analysis, assuming $n = 2$, gave the values for $A$ and $E$ listed in Table 1, column 2.

Comparison of the values for $A$ and $E$ in columns 1 and 2 of Table 1 shows that the inclusion of the temperature and concentration dependences of $C_{\mathrm{P}}$ leads to only small changes in the Arrhenius kinetic parameters evaluated for the esterification reaction.

### *3.3 Isothermal data*

#### 3.3.1 Exothermicity

$\Delta H$ is determined by heat-flow calorimetry by integrating the rate of heat generation (Eq. 1) until the $T_{\mathrm{j}}$ becomes equal $T_{\mathrm{r}}$ at reaction completion.

$$\Delta H=-\frac{1}{m_s}\int_{t_0}^{t_f}U\cdot S\cdot(T_{\mathrm{r}}-T_{\mathrm{j}})\cdot\mathrm{d}t \tag{6c}$$

A value of $\Delta H_{303} = 292.8\ \mathrm{kJ\cdot kg^{-1}}$ was obtained from the heat flow calorimetric data for the esterification reaction. This is in reasonable agreement with the values obtained from the adiabatic data (Table 1). (The evaluation of $\Delta H_{303}$ included some allowance for heat losses through the top of the reaction vessel.)

#### 3.3.2 Kinetic constants

The conversion at any instant can be calculated from the partial area:

$$x=\frac{-\int_{t_0}^{t}U\cdot S\cdot(T_{\mathrm{r}}-T_{\mathrm{j}})\cdot\mathrm{d}t}{m_s\cdot\Delta H} \tag{8c}$$

and the rate of conversion is given directly by:

$$\frac{\mathrm{d}x}{\mathrm{d}t}=-\frac{U\cdot S\cdot(T_{\mathrm{r}}-T_{\mathrm{j}})}{m_s\cdot\Delta H} \tag{8c}$$

Figure 7 shows the plot of rate against conversion determined from the isothermal heat flow calorimetric data for the esterification reaction (Fig. 5). The second order dependence of $dx/dt$ on $x$ (predicted by the simple interpretation of adiabatic data) is also plotted in Fig. 7 for comparison.

It is clear from Figs 5 and 7 that simple *n*th order kinetics cannot describe satisfactorily the temporal evolution of the rate of heat generation at constant temperature. It is evident from the initial increase in the difference between $T_r$ and $T_j$ that the process is autocatalytic. The autocatalytic effect is probably associated with the production of propionic acid. Some evidence for this can be seen from studies of the hydrolysis of acetic anhydride [7, 8]. The rate of hydrolysis ( analogous to esterification) in aqueous solution was influenced only slightly by the addition of sulphuric acid, but, in acetic acid solution, sulfuric acid was an effective catalyst.

## 4. Characterisation of an autocatalytic exothermic reaction by combined interpretation of isothermal and adiabatic data

### *4.1 Temperature dependence*

Re-writing Eq. (2) in a more generalised form (to admit the possibility of autocatalysis, while retaining the assumption that the temperature and concentration dependence of reaction rate are separable) gives:

$$\frac{dx}{dt} = k_T f(x) \tag{10}$$

from Eq. (10), retaining the assumption of Arrhenius temperature dependency for $k_T$, the adiabatic and isothermal data can be compared, at corresponding values of $x$, using:

$$\frac{(dx/dt)_{ad}}{(dx/dt)_{is}} = \frac{k_T f(x)}{k_{T_{is}} f(x)} = \frac{\exp(-E/RT)}{\exp(-E/RT_{is})} \tag{11}$$

and a plot of $\ln\left(\frac{(dx/dt)_{ad}}{(dx/dt)_{is}}\right)$ *vs.* $\frac{1}{T}$ will give a straight line of gradient $-E/R$ if the assumptions are valid. This procedure has been applied to the calorimetric data for the esterification reaction. Reasonable linear correlation was obtained (correlation coefficient 0.97). The corresponding value of $E$ is given in Table 1 (column 3).

The validity of this procedure can be examined by substituting the value of $E$ in Eq. (11) and predicting isothermal rates of conversion from the adiabatic data. Figure 7 shows a comparison between the results of the isothermal experiment and isothermal rates of conversion predicted using the adiabatic self-heat rate data. Some discrepancies can be seen between the measured isothermal rates and those extrapolated from adiabatic data. These discrepancies are associated with shortcomings in the above assumptions and with experimental errors associated with the measurement of very high or very low rates of heat generation. However, considering the temperature range involved, the discrepancies are not large and the assumption of a single activation energy and a reaction mechanism independent of temperature is tenable.

### *4.2 Concentration dependence*

Theoretical prediction of the magnitude of the autocatalytic effect and the form of $f(x)$ is difficult because of uncertainties as to the reaction mechanism and the complex interaction between sulphuric acid and propionic acid. The influence of sulphuric acid concentration on the kinetics of esterification will be discussed elsewhere. The following rate equation is proposed in order to account for the isothermal calorimetric data for the mixture containing 0.8% sulphuric acid:

$$\frac{dx}{dt} = (1-x)^2 \left( \frac{x}{B-\sqrt{x}} + C \right) A \exp\left( \frac{-E}{RT} \right) \tag{12}$$

Values for the constants $A$, $B$ and $C$ have been determined by nonlinear regression analysis of the isothermal rates of conversion including both isothermal calorimetric data and rates extrapolated from adiabatic self-heat rate measurements (with equal weighting). These values of $A$, $B$ and $C$ are listed in Table 1 (column 3) and the corresponding fitted curves (adiabatic and isothermal) are plotted in Figs 2 and 7 for comparison with the experimental data.

It is particularly noteworthy that the inclusion of the autocatalytic term in Eq. (12) does not preclude a good fit to adiabatic data for which the previous analysis had strongly indicated a simple second order concentration dependence. Conversely, the above analysis has demonstrated that reliance solely on adiabatic data can result in complete failure in the determination of the concentration dependence of the rate of heat generation.

## 5. Simulation

In order to explore the consequences of different interpretations of thermoanalytical data a mathematical simulator [9] has been used to predict temperature-time profiles when the esterification reaction is carried out in a jacketed chemical reactor. These are compared with experimental data which showed how the esterification reaction can proceed to thermal runaway in the RC1 reaction calorimeter operating in isoperibolic mode. Simulated curves have been produced based on the simple second order kinetic model which would be derived from adiabatic data interpreted in isolation, (but including the variation of $C_p$ with

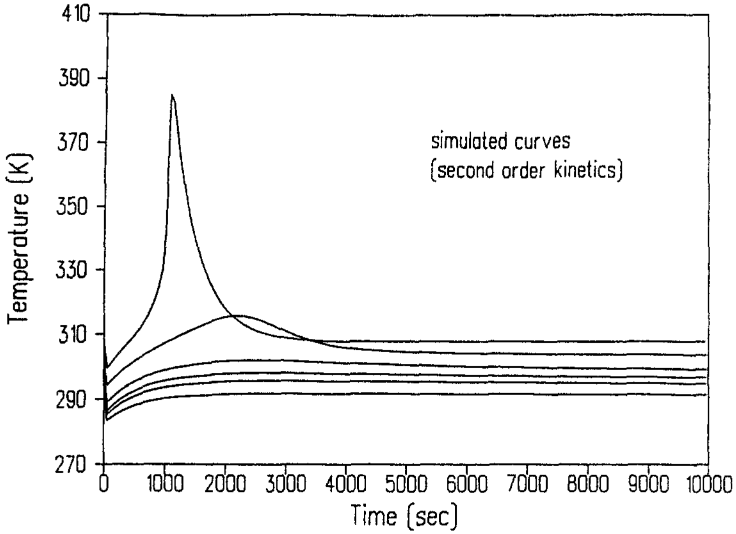

**Fig. 8** Temperature-time profiles simulated assuming second order kinetics for esterification reaction at a series of jacket temperatures corresponding to those for the experimental curves (Fig. 5)

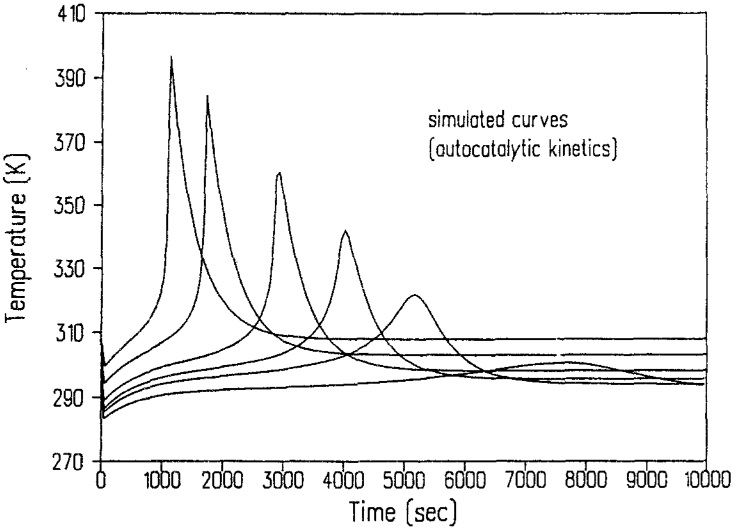

**Fig. 9** Temperature-time profiles simulated assuming autocatalytic kinetics for esterification reaction at a series of jacket temperatures corresponding to those for experimental curves (Fig. 5)

temperature and extent of reaction). These results are plotted in Fig. 8 for jacket temperatures corresponding to those used experimentally. A second set of simulated curves (Fig. 9) was produced based on the autocatalytic kinetic model which takes account of both the adiabatic and isothermal data. The simulations differed only in the kinetic model (and jacket temperature). Otherwise, identical starting conditions, physical properties and heat transfer coefficients were used.

Figures 8 and 9 demonstrates the important influence of autocatalysis on the progress of the reaction in a batch reactor. The experimental temperature-time profiles correspond closely to those predicted using a kinetic model which includes the autocatalysis. In particular, the simple second-order model completely fails to predict the significant excursions in reactor temperature which occurred when the jacket was maintained at temperatures between 300.7 K and 293.9 K. The simple kinetic model predicts critical conditions for exothermic runaway only when the jacket temperature exceeds 303.2 K.

The salient features of the temperature-time profiles predicted assuming second order and autocatalytic kinetics are compared in Table 2.

**Table 2** Comparison of the temperature-time profiles predicted assuming simple second order and autocatalytic rate equations for the esterification reaction in a jacketed reactor under conditions around those which lead to exothermic runaway

| Second order | Autocatalytic |
|---|---|
| underestimate of critical jacket temperature by approximately 10 K | predicts significant temperature excursions which occur at relatively low jacket temperatures |
| predicts sharp transition from subcritical to supercritical (runaway) conditions | indicates reduced parametric sensitivity with progressive increase in severity of runaway |
| relatively short times to maximum rate | long induction times predicted when system is marginally supercritical |

## 6. Conclusion

The foregoing discussion has demonstrated the importance of careful interpretation of calorimetric data when assessing the risk of exothermic runaway. It has been shown that a range of thermoanalytical techniques should be used to investigate the reaction under adiabatic and isothermal conditions. The example chosen involves only relatively simple chemistry with readily available data on the physical properties of reagents and products. Many industrial processes involve complex reactions where data on physical properties are not readily obtainable. Large safety margins and a circumspect appraisal of experimental data should be applied in such cases.

## Notation

| Symbol | Quantity | Units |
|---|---|---|
| $A$ | pre-exponential factor | $s^{-1}$ |
| $E$ | activation energy | $kJ\cdot mol^{-1}$ |
| $C_p$ | specific heat capacity of sample | $kJ\cdot kg^{-1}\cdot K^{-1}$ |
| $C_{pc}$ | specific heat capacity of sample container | $kJ\cdot kg^{-1}\cdot K^{-1}$ |
| $C_{pp}$ | specific heat capacity of products | $kJ\cdot kg^{-1}\cdot K^{-1}$ |
| $C_{pr}$ | specific heat capacity of reactants | $kJ\cdot kg^{-1}\cdot K^{-1}$ |
| $k_T$ | reaction rate constant | $s^{-1}$ |
| $n$ | order of reaction | |
| $m_c$ | mass of container | kg |
| $m_s$ | mass of sample | kg |
| $q_g$ | rate of heat generation | $kJ\cdot s^{-1}$ |
| $R$ | universal gas constant | $kJ\cdot mol^{-1}\cdot K^{-1}$ |
| $S$ | surface area | $m^2$ |
| $t$ | time | s |
| $t_o$ | onset time (isothermal data) | s |
| $t_f$ | final time (isothermal data) | s |
| $T$ | temperature | K |
| $T_f$ | final temperature (adiabatic data) | K |
| $T_i$ | initial temperature (adiabatic data) | K |
| $T_j$ | jacket temperature (isothermal data) | K |
| $T_r$ | reactant temperature (isothermal data) | K |
| $U$ | heat transfer coefficient | $W\cdot m^{-2}\cdot K^{-1}$ |
| $x$ | conversion (fraction of original substance converted to product) | |
| $\Delta T_{ad}$ | adiabatic temperature rise (instrumental) | K |
| $\Delta H$ | heat of reaction | $kJ\cdot kg^{-1}$ |
| $\Phi$ | thermal dilution factor | |

subscripts

| | |
|---|---|
| ad | adiabatic |
| is | isothermal |

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**Zusammenfassung** — Anhand einer einfachen Veresterungsreaktion wurden Standardverfahren zur Ermittlung thermokinetischer Parameter exothermen Reaktionen aus adiabatischen kalorimetrischen Daten demonstriert. Dabei wurde der Einfluß von Temperatur und Konzentration auf Änderungen der Wärmekapazität untersucht. Fehler bei der einfachen Interpretation adiabatischer Daten wurden identifiziert und isotherme Wärmeflußkalorimetrie wurde angewendet, um autokatalytische Effekte aufzuzeigen, die sich anhand der adiabatischen Experimente nicht ersehen lassen. Es wurde eine gründlichere Interpretation adiabatischer und isothermer Daten umrissen und verwendet, um die Bedingungen vorherzusagen, die in einem Kesselreaktor zu einem exothermen Davonlaufen der Reaktion führen. Mathematische Simulation der Bedingungen in einem Mantelkessel wurde angewendet, um zu zeigen, von welch großer Bedeutung die Entwicklung zuverlässiger kinetischer Ausdrücke ist, bevor man die Sicherheit einer Reaktion in einem Kesselreaktor beurteilt.