Journal of Thermal Analysis and Calorimetry, Vol. 66 (2001) 815–826

ON-LINE CALIBRATION AND DETERMINATION OF THE HEAT OF REACTION FOR LABORATORY SCALE HEAT TRANSFER CALORIMETERS

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(Received December 18, 2000; in revised form June 11, 2001)

Abstract

A simple method for the on-line calibration, in which both the heat transfer coefficient and the heat capacity of the reactor contents are determined, is described for laboratory scale heat transfer calorimeters. The calorimeter is operated in the isoperibolic mode for the calibration and a constant power is supplied to a resistor placed inside the reactor. The reactor heat balance differential equation is used to produce a set of linear simultaneous equations with each data acquisition cycle giving one equation. The heat transfer coefficient and the heat capacity are obtained from this set of equations by linear least squares. The application of the calibration procedure is illustrated by experiments in which the heat of reaction is determined on-line for a simulated reaction with first order kinetics and for the hydrolysis of acetic anhydride.

Keywords: calibration, hydrolysis of acetic anhydride, reaction calorimetry

Introduction

In reaction calorimetry it is desirable to monitor in as near to real time as possible the heat, rate and extent of the chemical reaction under study. The rate of reaction is related to the rate of heat production due to chemical reaction ($\dot{Q}_{\mathrm{chem}}$), while both the heat generated by the reaction (Q_{chem}) and the extent of reaction are related to the integral of $\dot{Q}_{\mathrm{chem}}$ with respect to time. In a computer controlled calorimeter it is, therefore, useful to determine $\dot{Q}_{\mathrm{chem}}$ and Q_{chem} on-line. In heat transfer calorimeters this requires knowledge of both the heat transfer coefficient (*UA*) and the heat capacity of the reactor contents (C_{p}) [1]. For cases where there are not significant changes in *UA* and C_{p} during the reaction, determination of *UA* and C_{p} (a calibration) before the start of the reaction is sufficient. When there are significant changes in *UA* or C_{p} recourse must be made to more sophisticated techniques such as temperature oscillation calorimetry [2].

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1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Commercial calorimeters such as the Mettler RC1 [3] or the HEL auto-MATE [4] provide an on-line determination of UA, but C_p has to be determined in an off-line data analysis. In both calorimeters a constant power supplied to a calibration resistor placed inside the calorimeter is used to determine UA. In the RC1 this is done with the calorimeter operating in the isothermal mode while in the auto-MATE this is done in the isoperibolic mode. The determination of C_p in the RC1 also requires an additional experimental step in which a temperature ramp is applied to the reactor. The auto-MATE C_p determination uses the approach to steady state behaviour after the power to the calibration resistor is switched on. In this paper it is shown that both UA and C_p can be determined on-line using the isoperibolic method.

The on-line calibration and determination of $\dot{Q}_{chem}$ and Q_{chem} is illustrated by two experiments with a calorimeter operating in the isoperibolic mode. In the first, after the calibration, the power to the calibration resistor is programmed to simulate a reaction with first order kinetics. The second experiment is the hydrolysis of acetic anhydride

$$(CH_3CO)_2O+H_2O\rightarrow 2CH_3COOH \tag{1}$$

a reaction which is used as a tutorial for the RC1 calorimeter [3].

Theory

In this section two sets of equations for determining UA and C_p are derived by integrating the reactor heat balance equation in the absence of a chemical reaction for an isoperibolic calorimeter. Although not suitable for an on-line determination these equations were used to check the on-line method which is described next. Finally, the reactor heat balance equation when there is a chemical reaction is considered in order to derive equations for $\dot{Q}_{chem}$ and Q_{chem}.

The heat balance differential equation for an isoperibolic reactor fitted with an internal heater in the absence of chemical reaction may be written as

$$C_p(\mathrm{d}^RT/\mathrm{d}t)=UA(^JT_0-{}^RT)+\dot{Q}_{loss}+P_{stirrer}+P \tag{2}$$

where $^JT_0$ is the constant jacket temperature, ^RT the reactor temperature, $\dot{Q}_{loss}$ the rate of heat loss from the reactor, $P_{stirrer}$ is the rate of heat production due to stirring and P is the rate of heat production by the heater. If the reactor is initially assumed to be operating in a steady state with zero heater power

$$0=UA(^JT_0-{}^RT_0)+\dot{Q}_{loss}+P_{stirrer} \tag{3}$$

Substitution of Eq. (3) into Eq. (2) with the assumptions of constant heat loss and stirrer power gives

$$\mathrm{d}^RT/\mathrm{d}t+\beta^RT-\beta^RT_0-P/C_p=0 \tag{4}$$

where

$$\beta=UA/C_p \tag{5}$$

Equation (4) is an ordinary linear differential Eq. (5) which can be integrated to give

$$^{\mathrm{R}}T={}^{\mathrm{R}}T_0+\frac{e^{-\beta t}}{C_\mathrm{p}}\int e^{\beta t}P(t)\mathrm{d}t+ce^{-\beta t} \tag{6}$$

where the constant of integration is determined by the form of the function $P(t)$ and the condition that at $t=0\,{}^{\mathrm{R}}T={}^{\mathrm{R}}T_0$.

If the reactor heater is switched on at $t=0$ with a constant power P_0 Eq. (6) becomes

$$^{\mathrm{R}}T={}^{\mathrm{R}}T_0+\frac{P_0(1-e^{-\beta t})}{UA} \tag{7}$$

Equation (6) can also be written as

$$\ln\left(1-\frac{({}^{\mathrm{R}}T-{}^{\mathrm{R}}T_0)UA}{P_0}\right)=-\beta t \tag{8}$$

When the reactor reaches a steady state

$$UA=\frac{P_0}{{}^{\mathrm{R}}T_\mathrm{ss}-{}^{\mathrm{R}}T_0} \tag{9}$$

where ${}^{\mathrm{R}}T_\mathrm{ss}$ is the final steady state reactor temperature. Equation (9) may be used to derive UA and then Eq. (8) to obtain β and then with Eq. (5) C_P. This is similar to the method used in the auto-MATE calorimeter except that here an analytical expression (Eq. (8)) is used to obtain C_p rather than numerical integration of the heat balance differential equation.

Alternatively, one can write

$$^{\mathrm{R}}T={}^{\mathrm{R}}T_0 \quad (t_0\leq t) \tag{10}$$

$$^{\mathrm{R}}T={}^{\mathrm{R}}T_0+\frac{P_0(1-e^{-\beta(t-t_0)})}{UA} \quad (t\geq t_0) \tag{11}$$

where t_0 is now the time when the power to the heater is switched on. Equations (10) and (11) can be used in a non-linear least squares fitting procedure (6) in which the parameters to determine are UA, C_p, ${}^{\mathrm{R}}T_0$ and t_0. Switching off the power to the calibration resistor can be regarded as switching on a power of $-P_0$. The equations given above can also be used for a second calibration when the power is switched off by replacing P_0 by $-P_0$. These two methods are not convenient for an on-line calibration because they need to keep a relatively large amount of data available and the second method needs iterative non-linear least squares fitting.

For a particular time, t, after the power to the heater has been switched on Eq. (4) can be written as

$$({}^{\mathrm{R}}T-{}^{\mathrm{R}}T_0)_\mathrm{t}UA+(\mathrm{d}{}^{\mathrm{R}}T/\mathrm{d}t)_\mathrm{t}C_\mathrm{p}=P_0 \tag{12}$$

Equation (12) can be regarded as a member of a set of linear simultaneous equations in UA and C_p. When the number of equations in this set is greater than two, UA and C_p may be obtained by linear regression (least squares) (7) to give

$$UA=(dc-eb)/D \tag{13}$$

$$C_p=(ae-bd)/D \tag{14}$$

where

$$D=ac-b^2 \tag{15}$$

and

$$a=\sum({}^{R}T-{}^{R}T_0)_t^2 \tag{16}$$

$$b=\sum({}^{R}T-{}^{R}T_0)_t(\mathrm{d}^{R}T/\mathrm{d}t)_t \tag{17}$$

$$c=\sum(\mathrm{d}^{R}T/\mathrm{d}t)_t^2 \tag{18}$$

$$d=P_0\sum({}^{R}T-{}^{R}T_0)_t \tag{19}$$

$$e=P_0\sum(\mathrm{d}^{R}T/\mathrm{d}t)_t \tag{20}$$

This approach is well suited for on-line determination as the summations of Eqs (16)–(20) can be updated on each cycle of data acquisition and also the evolution of the values of UA and C_p can be followed. As above, a second calibration can be made when the heater power is switched off if P_0 is replaced by $-P_0$ in Eqs (19) and (20).

The implementation of the calibration and the determination of $\dot{Q}_{\mathrm{chem}}$ and Q_{chem} require the determination of $(\mathrm{d}^{R}T/\mathrm{d}t)_t$. This may be done using the method of Savitzky and Golay [8] for smoothing and differentiation of data in which the interval between points is constant. This method assumes that the data in a small segment centred about point where it is required to calculate the smoothed value or the derivative can be represented by a polynomial which can be determined from the data in the segment by least squares. The smoothed value of, for example, the reactor temperature and its time derivative are expressed in the form

$$({}^{R}T)_{\mathrm{smoothed}}=\frac{\sum_{i=-m}^{m}n_i({}^{R}T)_i}{N} \tag{21}$$

$$(\mathrm{d}^{R}T/\mathrm{d}t)_{i=0}=\frac{\sum_{i=-m}^{m}n_i'({}^{R}T_i)}{N'\Delta t} \tag{22}$$

where the n_i and n_i' are convoluting integers and the N and N' are normalising integers which have been tabulated by Savitzky and Golay [8]. In this work an eleven point smoothing interval (m=5) and a third order polynomial with an interval between data acquisition cycles (Δt) of 6 s have been used. The determination of the smoothed values of ${}^{R}T$ and its time derivative therefore lag behind real time by 30 s. It has also been found better to start the summations of Eqs (16)–(20) $2m$+1 points after the heater power has been switched on or off.

The experiments to illustrate the on-line determination of $\dot{Q}_{\text{chem}}$ and Q_{chem} have been made with the calorimeter operating in the isoperibolic mode. With the assumptions of constant heat loss and stirrer power the differential heat balance equation is

$$\mathrm{d}^{\mathrm{R}}T/\mathrm{d}t - \beta^{\mathrm{R}}T + \beta^{\mathrm{R}}T_0 - \dot{Q}_{\text{chem}}/C_{\mathrm{p}} = 0 \tag{23}$$

and this can be rearranged to give

$$\dot{Q}_{\text{chem}} = ({}^{\mathrm{R}}T - {}^{\mathrm{R}}T_0)UA + (\mathrm{d}^{\mathrm{R}}T/\mathrm{d}t)C_{\mathrm{p}} \tag{24}$$

The heat of reaction as a function of time is

$$Q_{\text{chem}} = UA\int({}^{\mathrm{R}}T - {}^{\mathrm{R}}T_0)\mathrm{d}t + C_{\mathrm{p}}\int(\mathrm{d}^{\mathrm{R}}T/\mathrm{d}t)\mathrm{d}t \tag{25}$$

In the first example used to demonstrate the on-line method, after the calibration, the power to the resistor inside the reactor was programmed to simulate a first order reaction with

$$\dot{Q}_{\text{chem}} = P(t) = P_0 e^{-\mathrm{k}_1 \mathrm{t}} \tag{26}$$

The power delivered to the resistor was determined by measuring the current and voltage on each data acquisition cycle and so it was possible to have a direct comparison with the values of $\dot{Q}_{\text{chem}}$ calculated from the values of UA and C_{p} using Eq. (24). Substitution of Eq. (26) for $\dot{Q}_{\text{chem}}$ into Eq. (23) leads to a differential equation that can be integrated using Eq. (6) to give

$${}^{\mathrm{R}}T = {}^{\mathrm{R}}T_0 + \frac{P_0}{C_{\mathrm{p}}(\beta - k_1)}(e^{-\mathrm{k}_1\mathrm{t}} - e^{-\beta\mathrm{t}}) \tag{27}$$

Equation (27) can be used to compare the experimental and theoretical reactor temperature profiles for the simulated reaction. The total heat generated in the simulated reaction (Q_{sim}) can be determined by integrating Eq. (26) with respect to time and is

$$Q_{\text{sim}} = \frac{P_0}{k_1(1 - e^{-\mathrm{k}_1\mathrm{t}})} \tag{28}$$

Experimental

The simple calorimeter used in this work has been assembled from readily available components and a schematic diagram is shown in Fig. 1. The 0.5 L glass reactor is fitted with an IKAVISC MR D1 stirrer, a platinum (Pt-100) resistance thermometer (Jumo A.N. 90) and a 25 ohm resistance heater (Z. R. E. s. r. l.). Platinum resistance thermometers are also located at the entrance to and exit from the reactor jacket and also in the bath of the circulating thermostat (Haake F3) which is used to circulate the heating/cooling fluid. The platinum resistance thermometers are connected via a Keithley 2000 scanner card to a Keithley 2000 multimeter. Voltages related to the

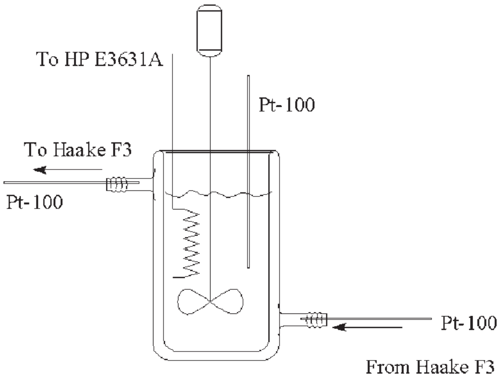

Fig. 1 Schematic diagram of the calorimeter used in this work

stirrer speed and torque coming from the stirrer controller are also read by the multimeter. The reactor heater is connected to a Hewlett Packard HP E3631 A programmable power supply which can also measure the current and voltage at its output. Both the multimeter and power supply are interfaced to a 300 MHz Pentium II personal computer via a GPIB interface. The software required for data acquisition and instrument control was developed using the TestPoint [9] program. For internal consistency the platinum resistance thermometers were calibrated against each other and against the internal thermometer of a Julabo MH4 circulating thermostat fitted with a RS 232 computer interface.

Calibrations were made by adjusting the temperature of the Haake F3 circulating thermostat until the reactor reached the desired temperature. After the calorimeter had reached a steady state as indicated by the nearly constant value of the smoothed ^{R}T and small value of $(\mathrm{d}^{R}T/\mathrm{d}t)$ the determination of the average value $^{R}T_0$ was started and continued for 10–15 min. After this the heater power was switched on with P_0 typically in the range 10–15 W in order to have a temperature rise in the reactor of ~1°C. In the determination of UA and C_P 100 points were used. The system was again allowed to reach a steady state and then the averaging of ^{R}T was started. After about 10–15 min the power to the resistor was switched off and as before 100 points were used to determine UA and C_P. The values of UA and C_P used in the on-line determinations of $\dot{Q}_{\mathrm{chem}}$ and Q_{chem} were averages of the values for when the power to the resistor was switched on and off.

The experiment on the hydrolysis of acetic anhydride was made by filling the calorimeter with 370 mL of distilled water. A stoppered conical flask was filled with ~25 mL of 99% pure acetic anhydride (Aldrich), was weighed and then placed in the bath of the Haake F3, which was set to 25°C, in order to reach as near as possible the same temperature as the water in the calorimeter. After the calibration and the calorimeter had once again returned to a steady state the average temperature of the reactor was determined for 10–15 min. The flask was removed from the thermostat, its outside was wiped dry and the acetic anhydride was poured quickly into the calorimeter. At the same time, as the acetic anhydride was added to the calorimeter the determination of $\dot{Q}_{\mathrm{chem}}$ and Q_{chem} was started. The flask and stopper were reweighed and the mass of acetic anhydride added to the calorimeter was determined by difference. After the reaction was completed a second calibration was made.

Results

The experimental results of a calibration made with ~400 mL of water in the calorimeter at a temperature of 10°C are shown in Fig. 2. A comparison of the values of *UA* and C_p obtained by on-line and off-line calibrations is given in Table 1 for the experi-

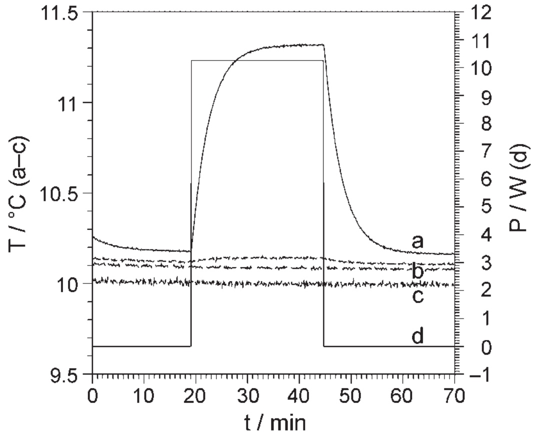

Fig. 2 The reactor temperature (a), the jacket inlet and outlet temperatures (b), the temperature of the thermostatic bath (c) and the power (d) supplied to the heater during a calibration

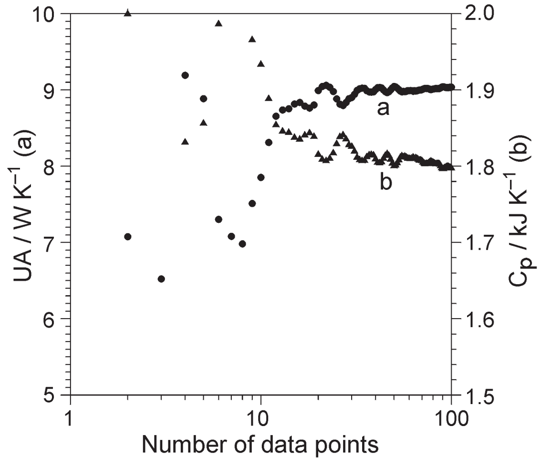

Fig. 3 The values of the heat transfer coefficient (*UA*) (a) and the heat capacity of the reactor contents (C_P) (b) depend on the number of data points used in the calibration

mental data illustrated in Fig. 2 and also for a calibration with the calorimeter filled with methanol at 25°C. The agreement between the on- and off-line data elaborations is very good. The low thermal capacity of methanol gives the calorimeter a lower relaxation time than when it is filled with water and, therefore, the calorimeter reaches steady state behaviour more rapidly. The dependence of the values of UA and C_p on the number of experimental points in an on-line calibration is shown in Fig. 3 where it can be seen that with only 20 points UA and C_p are within 10% of their final values.

Table 1 Comparison of on and off-line determinations of UA and C_P

	Resistor power on	Resistor power off
a) Water at 10°C		
on-line		
UA/W K^{-1}	9.00	8.90
C_p/kJ K^{-1}	1.804	1.805
Eqs (8) and (9)		
UA/W K^{-1}	9.07	8.93
C_p/kJ K^{-1}	1.818	1.805
Eqs (10) and (11)		
UA/W K^{-1}	9.03(1)[a]	8.89(1)
C_p/kJ K^{-1}	1.814(8)	1.816(8)
$^RT_0$/°C	10.182(1)	11.317(1)
t_0/s	4.4(1)	3.3(1)
b) Methanol at 25°C		
on-line		
UA/W K^{-1}	7.86	7.83
C_p/kJ K^{-1}	0.954	0.959
Eqs (8) and (9)		
UA/W K^{-1}	8.02	7.91
C_p/kJ K^{-1}	0.967	0.994
Eqs (10) and (11)		
UA/W K^{-1}	8.01(1)	7.92(1)
C_p/kJ K^{-1}	0.953(6)	0.982(7)
$^RT_0$/°C	24.992(1)	26.285(1)
t_0/s	2.9(5)	3.0(6)

[a] three standard errors in units of the least significant digit

The experimental and theoretical reactor temperature profiles and their difference for the experiment in which the power to the calibration heater was programmed to simulate a first order reaction are shown in Fig. 4a. The power supplied to the resistor was expressed by Eq. (26) with P_0=20.39 W and k_1=7.70·10^{-4} s^{-1}. The value of k_1 corresponds to a half-life of 15 min. The theoretical temperature profile was calculated using Eq. (27), with UA=10.06 W K^{-1} and C_P=1.819 kJ K^{-1} as obtained in the on-line calibration. The maximum difference between the observed and calculated reactor temperatures is ~ –0.05°C and occurred when the power to the heater was switched on. The standard deviation of the difference between the observed and calculated reactor temperatures is 0.008°C showing that the behaviour of the calorimeter is well accounted for theoretically. Figure 4b shows a comparison of the power supplied to the resistor (calculated from the product of the measured voltage and current measurements) with the values of '$\dot{Q}_{\mathrm{chem}}$' calculated on-line. This figure also shows a comparison of the heat generated by the resistor with 'Q_{chem}' determined on-line. The values of the quantities determined on-line lag behind those of the measured power supplied to the resistor by 0.5 min which is half the interval of time used in the

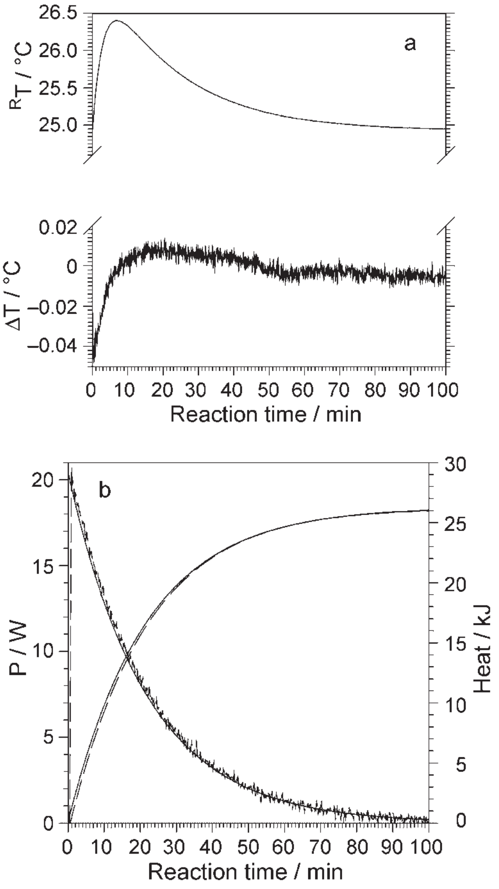

Fig. 4 The observed reactor temperature (a) and the difference between the observed and calculated reactor temperatures the measured and calculated power and heat generated by the resistor during a simulated first order reaction (b)

smoothing and differentiation of the reactor temperature. The value of the energy supplied to the resistor up to a time of 100 min calculated from Eq. (28) is 26.2 kJ and may be compared to the value 26.0 kJ calculated by the numerical integration of the power supplied to the resistor in that time and to the same value of Q_{chem} calculated on-line by the software. The value of Q_{sim} for an infinite time is 26.5 kJ. The $\dot{Q}_{\mathrm{chem}}$ *vs.* the reaction time curve (corrected for the delay) for reaction times greater 2 min was fitted to Eq. (26) giving P_0=20.6(3) W and k_1=7.71(1)·10^{-4} s^{-1} in excellent agreement with the values used to programme the power applied to the resistor.

The on-line values of $\dot{Q}_{\mathrm{chem}}$ and Q_{chem} for the hydrolysis of 0.26 mol of acetic anhydride in 20.6 mol of water at 25°C, calculated with the values of UA=9.92 W K^{-1} and C_p=1814 J K^{-1} obtained from a calibration before the start of the reaction are shown in Fig. 5. A calibration after the reaction gave UA=10.02 W K^{-1} and C_p=1789 J K^{-1}. The values of $\dot{Q}_{\mathrm{chem}}$ and Q_{chem} calculated with these values of UA and C_p on the scale of Fig. 5 are indistinguishable from the on-line values. The final value of Q_{chem} gives a value of $\Delta_r H$ of –60.8 kJ mol^{-1} for the enthalpy of reaction. This may be compared with the value of –60.6 kJ mol^{-1} obtained from the tabulated standard enthalpies of formation of –624.4 kJ mol^{-1} for acetic anhydride [10], –285.8 kJ mol^{-1} for water [11a] and –485.4 kJ mol^{-1} for the enthalpy of formation of aqueous acetic acid at the mole fraction of the present experiment (x=0.02) [11b].

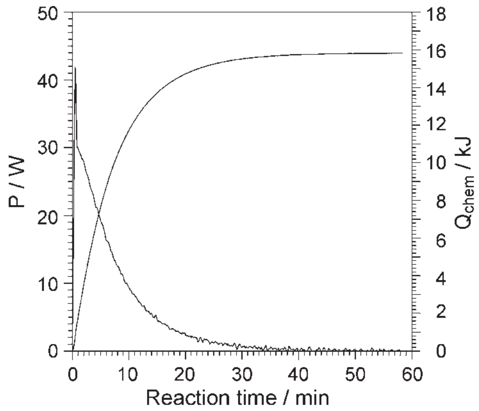

Fig. 5 The rate of chemical heat production ($\dot{Q}_{\mathrm{chem}}$) (a) and the heat of reaction (Q_{chem}) (b) for the hydrolysis of acetic anhydride at 25°C

The kinetics of the hydrolysis of acetic anhydride was much studied in the first half of the last century. Gold [12] as well as making extensive measurements also reviewed the earlier work and concluded that the reaction obeyed second order kinetics, being first order with respect to both acetic anhydride and water. Under the conditions of the present experiment the concentration of water is almost constant and the reaction has pseudo-first order kinetics. In the following it will be assumed that the departure from isothermal behaviour of the reacting system can be neglected as the maximum temperature rise in the reactor was ~2°C. The observed $\dot{Q}_{\mathrm{chem}}$ *vs.* *t* profile is very different from that of Fig. 4b at the start of the reaction. The first part of the profile is attributed to a rapid exothermic mixing of acetic anhydride and water and this is followed by the slower exothermic reaction. The $\dot{Q}_{\mathrm{chem}}$ *vs.* *t* profile of Fig. 5, after 10 min was fitted to Eq. (26) giving P_0=34.9 W and k_1=2.23·10^{-3} s^{-1}. Gold [12] gives a value of the pseudo-first order rate constant of k_1=2.63 10^{-3} s^{-1} at 25°C and the value obtained here is in good agreement with this. By extrapolating the calculated $\dot{Q}_{\mathrm{chem}}$ curve back to *t*=0 and taking the difference between this and the observed curve it is possible to separate the contribution of the mixing from that of the reaction. Integration of this difference between the times that the two curves intersect gives a value of 0.1–0.3 kJ for the heat of mixing and this corresponds to an enthalpy of mixing of –0.8(4) kJ mol^{-1}.

Conclusions

This work shows that both the heat transfer coefficient and the heat capacity of the reactor contents can easily be determined on-line for heat transfer calorimeters. For chemical reactions where there are not significant changes in *UA* and C_p this makes it possible to determine more precisely on-line the rate of heat production and the heat of chemical reaction compared to calorimeters which use a calibration procedure in which only *UA* is determined on-line. This is important when the calorimeter is operated in the isoperibolic mode. A more precise on-line determination can also save time since it can avoid off-line data analysis after the experiment to a certain extent.

This work illustrates the usefulness of the Savitzky and Golay method [8] for smoothing and differentiating data on-line since it requires relatively small segments of data and is non-iterative. The time lag in presenting the derived $\dot{Q}_{\mathrm{chem}}$ and Q_{chem} is 30 s in the present experiments. It appears to be well suited to a calorimeter operating in the isoperibolic mode. The experiment on the hydrolysis of acetic anhydride shows that an isoperibolic calorimeter can be used to separate the heat of mixing from that of reaction in suitable circumstances.

List of symbols

a, b, c, d, e	summations involved in the least squares determination of *UA* and C_P
D	determinant involved in the least squares determination of *UA* and C_P
C_P	heat capacity of the reactor contents in J K^{-1}
k_1	first order reaction rate constant in s^{-1}
n_i, n_i'	Savitzky–Golay convoluting integers
N, N'	Savitzky–Golay normalizing integers
$P(t)$	power applied to the calibration resistor in W
P_0	initial or constant power applied to the calibration resistor in W
P_{stirrer}	power dissipated through stirring the reactor contents in W
Q_{chem}	heat produced by chemical reaction in J

$\dot{Q}_{\mathrm{chem}}$	rate of heat production by chemical reaction in W
$\dot{Q}_{\mathrm{loss}}$	rate of heat loss from the calorimeter in W
Q_{sim}	heat produced in a simulated chemical reaction in J
t, t_0	time, time when the heater power was switched on or off in s
$^{\mathrm{J}}T_0$	the constant jacket temperature in °C
$^{\mathrm{R}}T$	reactor temperature in °C
$^{\mathrm{R}}T_0$	initial reactor steady state temperature in °C
$^{\mathrm{R}}T_{\mathrm{ss}}$	final reactor steady state temperature in °C
UA	reactor heat transfer coefficient in W K^{-1}
x	mole fraction of solute
β	ratio of UA to C_P in s^{-1}
$\Delta_r H$	enthalpy of reaction in kJ mol^{-1}
Δt	interval between data acquisition cycles in s

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