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Dynamic measurements by heat flux calorimetry

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Abstract

A simple procedure for the deconvolution of signals from a heat flux calorimeter has been tested using the hydrolysis of *tert*-butyl chloride as a test reaction. Satisfactory results have been obtained even when the half-life of the reaction was as short as about twice the response time of the calorimeter. The results provide some guidance in the selection of correction parameters for various experimental configurations.

INTRODUCTION

In a previous publication [1] we reported the calibration of the Setaram heat flux calorimeter (model C80) and its use to study the low temperature, slow decomposition of *tert*-butyl peroxybenzoate. We have now investigated the use of the calorimeter for moderately fast reactions where it becomes important to make adequate allowance for the slow response of the equipment. The basis of making such an allowance lies in a knowledge of the response characteristics of the equipment which we have determined using electrical pulse heating experiments.

The Setaram heat flux calorimeter bears some resemblance to conventional differential scanning calorimeters: it is differential in operation with two matched reaction vessels in cylindrical cavities side-by-side in a calorimetric block. The two cavities are surrounded by thermopiles and the instrument signal is derived from the difference between the e.m.f. generated in the thermopiles. The temperature of the calorimetric block can be programmed to increase or decrease at a linear rate. An important feature of the instrument is its high thermal stability. This is achieved at the expense of a response time considerably greater than for conventional thermal analysers. A time of about 300 s was indicated in experiments in which an electrical calibration heater was switched on and off. Only for very slow reactions can signal correction be neglected.

The hydrolysis of *tert*-butyl chloride has been used as a test reaction. The rate constant of the reaction has been derived from calorimetric experiments and the value compared with that obtained using a more conventional approach where the response time is negligible. The measurements have been carried out using two types of mixing vessels both manufactured by Setaram. In one, the reaction vessel is divided into two compartments, one above the other, by a Teflon septum. The components are placed separately in the two compartments and the reaction started by piercing the septum with a stirrer. In the other type of reaction vessel the lower compartment is closed by a lid and sealed with mercury. The reaction is started by rotating the entire calorimeter through 180 °. A desirable feature is that the response characteristics should not be strongly dependent on the reaction vessel and sample. This is an aspect which we have been concerned to investigate together with alternative procedures for obtaining the correction parameters.

EXPERIMENTAL

The electrical pulse heating experiments were carried out using the equipment described in ref. 1.

The *tert*-butyl chloride used in the hydrolysis experiments was 98% pure (BDH). The experiments were carried out by adding the butyl chloride to a mixture of water and acetone. Different rates of reaction were obtained by varying the relative amounts of water and acetone. In most of the experiments 0.1 cm^3 *tert*-butyl chloride was used with 3 cm^3 of a mixture containing 60% water and 40% acetone by volume.

The *tert*-butyl chloride was placed in the lower compartment of the reaction vessels and the water/acetone mixture in the upper compartment. With the stirrer vessel, the reaction mixture was stirred by rotating the stirrer ten times after piercing the septum. With the other reaction vessel the calorimeter was rotated four times. The reference cell contained only the water/acetone mixture in the upper compartment. Otherwise the procedure with the reference vessel was the same as that with the vessel containing the reaction mixture. In this way the effect of the enthalpy change associated with mixing, stirring and rotating the calorimeter was largely eliminated from the instrument signal. The signal was recorded as 3000 data points using an Amstrad computer (model 1640), a purpose-built low-noise amplifier and a 12-bit analogue-to-digital converter.

The hydrolysis experiment was also studied by measuring the conductivity of the reaction mixture using a platinum plate conductivity cell. The same samples of *tert*-butyl chloride and water/acetone mixture were used in the same relative amounts as in the calorimetric experiments and at the same temperature (303 K). The conductivity measurements were made in the presence of the steel reaction vessels and mercury when relevant. The measurements were carried out over a period of ten times the half-life of the reaction. The first-order rate constants were derived from straight line plots of $\ln(G_0 - G_t)$ against time t (correlation coefficients > 0.998) where

G_t and G_0 are the conductivities at time t and at the end of the reaction, respectively.

SIGNAL CORRECTION

The design of the C80 calorimeter is similar to that of a number of heat flux calorimeters manufactured by Setaram. The effect of the long response time with this type of equipment is to smear the signal produced by a thermal event in the calorimeter. This may be unimportant if the thermal event itself is very slow but in general it is necessary to correct the instrument signal to obtain a true record of the rate of the thermal event, i.e. the heat flux. In principle at least, the determination of the total enthalpy change from the area enclosed by the instrument signal does not pose a difficulty.

The starting point for the analysis is the equation

$$\mathrm{F} = K * W$$

$$\begin{aligned} F(t) &= \int_{-\infty}^{t} K(t-u)W(u)\,\mathrm{d}u \\ &= \int_{-\infty}^{t} K(u)W(t-u)\,\mathrm{d}u \end{aligned} \tag{1}$$

which relates the thermal flux measured experimentally, $F = F(t)$ at time t with the differential heat output $W = W(t) = -\mathrm{d}\Delta H/\mathrm{d}t$, where $\Delta H = H_\mathrm{s} - H_\mathrm{r}$, the subscripts s and r refering to the sample and reference. The object is to determine $W(t)$ from $F(t)$; $K(t)$ is the response function of the apparatus and $K(t) = F(t)$ for a unit impulse of W at time zero. We assume that the measuring system is linear—an assumption which was confirmed by the previous electrical calibration experiments. There are a number of routes to the required quantity. Fourier transform methods have been used but difficulties can arise from the need for smoothing. Here we use an asymptotic solution to the problem. The object is a simple procedure with known limits of validity. Assuming that the time scale of W is long compared with that of K we obtain the expansion

$$W(t) = F(t) + B_1F^1 + (B_1^2 - 0.5B_2)F^2 + \ldots \tag{2}$$

where

$$F^n = \mathrm{d}^nF(t)/\mathrm{d}t^n \quad \text{and } B_n = \int_0^\infty t^nK(t)\,\mathrm{d}t \tag{3}$$

For eqn. (2) to be useful, the terms F, B_1F^1, $(B_1^2 - 0.5B_2)F^2$ must become progressively smaller. In particular we must have F varying sufficiently slowly that $B_1F^1 < F$ or $B_1(\mathrm{d}\ln F)/\mathrm{d}t < 1$ is satisfied. B_1 and B_2 may be obtained from the experimental signal recorded when the calorimeter is electrically pulse heated. Alternatively, it may be more convenient to use constant electrical heating over long times in which case we may calculate the constants B_1 and B_2 using the relationships

$$B_1 = \int_0^\infty (t/h - \tfrac{1}{2}) S \, \mathrm{d}t$$

$$B_2 = \int_0^\infty ((t^2/h) - t + h/6) S \, \mathrm{d}t \tag{4}$$

where $h^{-1} \int_0^\infty S \, \mathrm{d}t = 1$.

In these expressions h is the time width of the heating and S is the observed curve $F(t)$. Implicit in these two approaches is the assumption that the response function $K(t)$ is constant from one experiment to another. In considering the validity of the approach we have compared the time of a thermal event with the response time of the calorimeter t_s. The response time was defined in ref. 1, $t_s = t_r = t_d$ where t_r and t_d are the rise and decay times of the exponential rise and decay of the instrumental signal when an electrical heater is switched on and off. The comparison is one of convenience with $t_s \approx 300$ s.

RESULTS AND DISCUSSION

The values of B_1 and B_2 calculated from the electrical pulse heating experiments are shown in Table 1. In principle the values should be derived from experiments in which the pulse of heat is delivered over an

TABLE 1

The values of the correction parameters derived from electrical heating experiments at 303 K

	Time (s)	B_1	$10^{-3}B_2$
Pulse heating [a]	1.5	297	159
	3.2	296	157
	6.0	295	159
	16.1	301	153
	35.2	312	153
Constant power [b]	2910.0	297	160
	1500.0	301	173
	1113.0	306	174
	599.7	310	176
	304.2	311	179
	150.1	311	169
	35.2	292	149

[a] B_1 and B_2 calculated from eqn. (3).

[b] B_1 and B_2 calculated from eqn. (4).

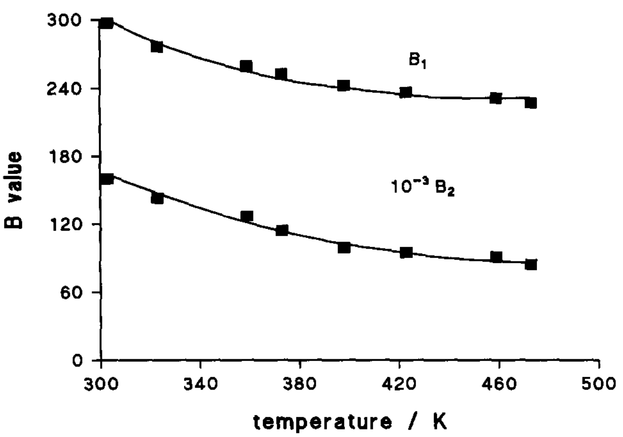

Fig. 1. The temperature dependence of the correction parameters B_1 and B_2 determined from experiments in which constant electrical heating was maintained for 3000 s.

infinitely short period (Dirac delta function). In practise the values are constant when the time of heating is < 6 s, i.e. less than 1/50 of the response time. Also shown in Table 1 are the values of B_1 and B_2 obtained using the alternative procedure in which a constant thermal power is supplied over long times. For times longer than about $10 \times t_s$, they agree with those obtained from the pulse heating experiments. Measurements have also been made with the calorimeter at different temperatures. The results are shown in Fig. 1. The values of B_1 and B_2 show a temperature dependence which is most marked at low temperatures.

We have examined the application of eqn. (2) to the deconvolution of the experimental curves obtained from the long-time heating experiments. We have used the values $B_1 = 297$ and $B_2 = 159 \times 10^3$. The results of the calculation are shown in Figs. 2 and 3. Rather surprisingly the method holds for times as short as about twice the response time. Over much of the correction procedure the ratio $B_1F^1/(B_1^2 - \frac{1}{2}B_2)F^2$ is greater than 10. Where F^1 and F^2 are large, when the heater current is switched on or off, the limitations in the approach are recognised as noise on the calculated signal. We have adopted some smoothing [2,3] in forming the first and second derivatives of the experimental signal.

The hydrolysis of butyl chloride has been used to examine the validity of the approach to chemical reactions. A comparison has been made between the kinetic results from the calorimetric experiments and those from the conductivity measurements. We have assumed that following deconvolution, the magnitude of the calorimetric signal is a measure of the rate of reaction. The rate constant was derived from graphs of $\ln(S/V)$ against time where S is the instrument signal measured in volts. The experiments were carried out with different relative amounts of water and acetone to vary the reaction rate. The results obtained using the stirrer reaction vessel

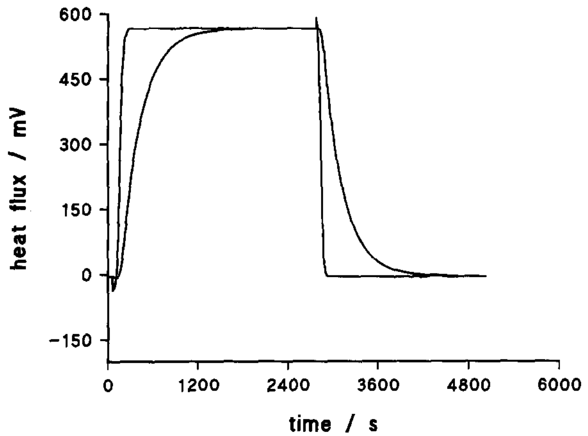

Fig. 2. The experimental and corrected curves for electrical heating maintained constant over a long time, $t \approx 10 \times t_s$.

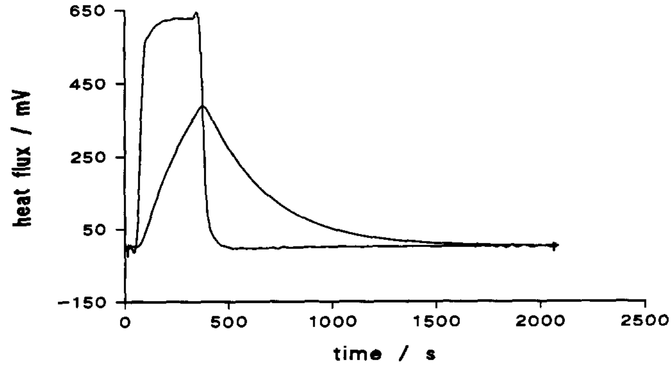

Fig. 3. The experimental and corrected curves for electrical heating maintained constant for about the response time.

TABLE 2

The kinetic rate constants obtained for the hydrolysis of *tert*-butyl chloride at 303 K

% Water	$t_{1/2}$ (s) [a]	$10^3\ k$ (s^{-1}) [a]	$10^3\ k$ (s^{-1}) [b]
100	50.2	13.8	6.34
90	70.3	9.86	4.51
80	116	5.97	3.68
70	237	2.92	2.45
60	513	1.35	1.36

[a] Conductivity measurements.

[b] Calorimetric measurements using stirrer vessels, $B_1 = 297$; $B_2 = 159 \times 10^3$.

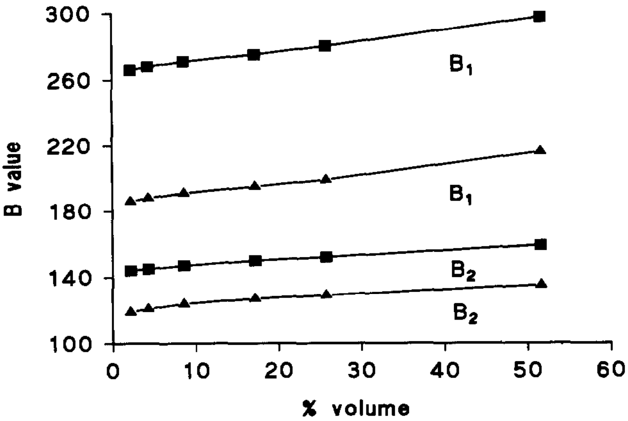

Fig. 4. The dependence of the correction parameters on the filled volume of the reaction vessels: ■, stirrer vessels; ▲, inversion vessels. Values of B_2 are to be multiplied by 10^3.

are shown in Table 2. We would expect the approach to hold when the reaction times were long but in practise the results indicate that the correction is valid even when the half-life is about equal to twice the response time. The correlation coefficient of the kinetic plots was > 0.99, consistent with first-order kinetics. In these experiments the reaction vessels were filled to about 50% of the total available volume. We have repeated the measurements filling the reaction vessels to different extents but maintaining the same relative amounts of the components. The values of B_1 and B_2 required to give the correct rate constant are shown in Fig. 4. The monatonic change in the values suggest that the response function depends on the extent to which the reaction vessels are filled, albeit to a small extent. Even so, correcting the data from an experiment in which the reaction vessel is 10% filled using the values of B_1 and B_2 applicable to the half-filled vessel leads to a rate constant $k = 2.91 \times 10^{-3}\ s^{-1}$, a discrepancy of about 10% from the correct value. Extrapolation of the curves in Fig. 4 leads to the values $B_1 = 263$ and $B_2 = 144 \times 10^3$ for the empty reaction vessels. The results obtained with the other mixing vessels are also shown in Fig. 4. The values of B_1 and B_2 are quite different from those for the stirrer vessels although they show the same trend with the volume. The values for the empty vessels are $B_1 = 183$ and $B_2 = 117 \times 10^3$. These values are consistent with the more rapid response obtained with these reaction vessels in spite of their greater mass. Mixing and stirring have been carried out sufficiently rapidly to avoid influencing the values of B_1 and B_2.

SUMMARY

The present recipe for correcting the experimental data obtained from the Setaram C80 calorimeter has the considerable advantage of simplicity.

Equation (2) allows a rapid assessment of the magnitude of the correction terms. For sufficiently long events with slowly moving signals, deconvolution may prove unnecessary. We have not attempted to investigate a third correction term but would rather not use the apparatus for the measurement of thermal power over times shorter than about twice the response time. The values of B_1 and B_2 obtained by electrical heating are not universally applicable to the different types of mixing vessels. The results point to a dependence of the response characteristics on the construction of the reaction vessels although for many experimental situations there is some indication of the likely magnitude of the correction parameters B_1 and B_2.

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