

FITTING ISOPERIBOLIC CALORIMETER DATA FOR REACTIONS WITH PSEUDO-FIRST ORDER CHEMICAL KINETICS

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The non-linear least squares fitting of the chemical heat flow and the reactor temperature are compared for reactions with pseudo-first order chemical kinetics carried out in an isoperibolic calorimeter operating quasi-isothermally. Both methods give very similar results for the reaction rate constant and enthalpy of reaction but fitting the reactor temperature appears to have some advantages especially when there is an enthalpy of mixing of the reagents.

Keywords: *isoperibolic reaction calorimeter, pseudo-first order chemical kinetics*

Introduction

In the classification of calorimeters [1, 2] the isoperibolic or constant jacket temperature reaction calorimeter is one of the simplest. This simplicity gives the isoperibolic calorimeter some advantages and some disadvantages over more sophisticated reaction calorimeters. Its principal advantage is that the heating/cooling power requirements and the circulating fluid flow rate necessary to keep the jacket temperature constant are less onerous than those for keeping the reactor temperature constant in an isothermal calorimeter. A serious disadvantage, unless special precautions are taken, is that for exothermic reactions a temperature increase of several °C may occur in the reactor and this complicates the analysis of the kinetics of a reaction or process since the temperature dependence of the reaction rate constants must be taken into consideration. With a suitable choice of reaction conditions it is often possible to limit the temperature rise in the reactor to ~1°C and the calorimeter can be considered to be operating quasi-isothermally. With suitably calibrated platinum resistance thermometers temperatures and temperature differences can be routinely determined to 0.01°C or better. Also, as will be seen below under conditions of constant rate of heat loss or gain from the surroundings and stirrer power dissipation only the temperature in the reactor is required. One method of achieving quasi-isothermal reaction conditions is to use a very large excess of one or more reagents. The concentration of a reagent in large excess can be considered to be effectively constant during the reaction and Ostwald's isolation method [3] can be applied with a considerable simpli-

fication in the analysis of the chemical kinetics. Many reactions proceed with pseudo-first order kinetics when this method is applied. One of the great advantages of isothermal calorimeters is that the differential equation or equations for the chemical kinetics can be integrated independently of the differential equation for the reactor energy balance.

In bench scale reaction calorimetry it is usual to derive information about the process thermodynamics and kinetics from the rate of heat production or consumption, the chemical heat flow [4]. Temperature is the fundamental measurement of calorimetry and it may be argued that it is preferable to obtain information by fitting to these measurements rather than to a derived quantity such as the chemical heat flow. This is simplified in the isoperibolic calorimeter since it is not necessary to take into consideration temperature control loops as would be necessary for isothermal calorimeters [5]. In this work the fitting of the chemical heat flow for reactions with pseudo-first order chemical kinetics in an isoperibolic calorimeter will be compared with the fitting of the temperature profile of the reactor.

Many chemical reactions are accompanied by an enthalpy change when the reagents are mixed. This change occurs very rapidly if the mixing is fast and in bench scale reaction calorimeters for endothermic mixing it often appears as a sharp decrease in the temperature of the reactor. This can create problems in determining the chemical heat flow at the start of the reaction and often the data pertaining to this part of the reaction are excluded from the data analysis. To a good approximation the mixing can be considered to occur adiabatically. Also, if it can be considered to

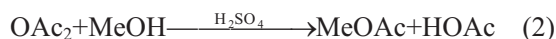
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occur instantaneously, in fitting the reactor temperature profile the initial temperature (T_i at $t=0$) can be considered as an additional parameter to be determined. This is particularly useful for an isoperibolic calorimeter when both the mixing and the reaction are exothermic.

Three types of experiment have been carried out in this work. In the first the chemical heat flow for a first order reaction was simulated by programming the power applied to the calibration resistor located in the reactor. The second type of experiments were the hydrolysis of acetic anhydride



carried out below room temperature where the mixing of the reagents is exothermic. The third type of experiment is the sulphuric acid catalysed esterification of acetic anhydride and methanol



carried out at 25°C where the mixing of the reagents is endothermic. Both the hydrolysis [6] and the esterification [7] can be considered to follow pseudo-first order chemical kinetics under the conditions used in this work.

Theory

The rate of chemical reaction for a reagent, A , that reacts with pseudo-first order kinetics is

$$\frac{d[A]}{dt} = -k[A] \quad (3)$$

where k is the reaction rate constant. This equation may also be written in terms of the conversion, X , as

$$\frac{dX}{dt} = k(1 - X) \quad (4)$$

Under isothermal conditions this equation may be integrated to give

$$X = 1 - \exp^{-kt} \quad (5)$$

The chemical heat flow, \dot{Q}_{chem} , is

$$\dot{Q}_{\text{chem}} = -\frac{n_A^0 \Delta_r H dX}{dt} \quad (6)$$

where n_A^0 is the initial amount of the reagent A and $\Delta_r H$ is the enthalpy of reaction. The negative sign is included in Eq. (6) in order to make the chemical heat flow positive for an exothermic reaction. Substitution of Eqs (4) and (5) into Eq. (6) gives

$$\dot{Q}_{\text{chem}} = -n_A^0 \Delta_r H k \exp^{-kt} \quad (7)$$

Rather than follow the traditional method of deriving the equations for the chemical kinetics and enthalpy of reaction for an isoperibolic calorimeter [8], a more chemical engineering approach will be adopted here. This emphasizes the similarities between bench scale reaction calorimeters and industrial batch reactors.

The differential equation for the reactor heat balance can be written in terms of the different heat flows as [9]

$$\dot{Q}_{\text{accum}} = \dot{Q}_{\text{trans}} + \dot{Q}_{\text{chem}} + \dot{Q}_{\text{loss}} + P_{\text{stirrer}} \quad (8)$$

where the rate of accumulation, \dot{Q}_{accum} , is given by

$$\dot{Q}_{\text{accum}} = C_p \frac{dT}{dt} \quad (9)$$

the chemical heat flow is given by Eq. (7), the rate of heat transfer between the reactor and jacket, \dot{Q}_{trans} , is

$$\dot{Q}_{\text{trans}} = UA(^J T - T) \quad (10)$$

while explicit expressions will not be given for the rate of heat exchange with the surroundings, \dot{Q}_{loss} , and the power dissipated by the stirrer, P_{stirrer} . In Eqs (9) and (10) T is the reactor temperature, $^J T$ is the jacket temperature, C_p is the heat capacity of the reactor contents and UA is the global heat transfer coefficient. In the following development C_p , UA , \dot{Q}_{loss} and P_{stirrer} will be considered to be constant.

If, before the reaction starts, the calorimeter is operating in a steady state with a reactor temperature T^0 , the reactor heat balance equation gives

$$\dot{Q}_{\text{loss}} + P_{\text{stirrer}} = -UA(^J T - T^0) \quad (11)$$

Substitution of Eq. (11) into Eq. (8) and rearrangement gives the following expression for the chemical heat flow

$$\dot{Q}_{\text{chem}} = C_p \frac{dT}{dt} + UA(T - T^0) \quad (12)$$

Equation (12) is used to determine the chemical heat flow from the experimental measurements and as mentioned in the introduction it does not contain the jacket temperature. In this work the algorithms of Savitsky and Golay [10] have been used for the smoothing and the differentiation of the reactor temperature.

Equation (12) can be rearranged to give a differential equation for the reactor temperature

$$\frac{dT}{dt} = \frac{\dot{Q}_{\text{chem}} - UA(T - T^0)}{C_p} \quad (13)$$

When Eq. (7) for the chemical heat flow is substituted into Eq. (13) the resulting linear first order equation can be integrated using the standard method [11]. If the initial condition is that the reactor temper-

ature is equal to its steady state temperature, i. e. there is no enthalpy change on mixing the reagents, the following equation is obtained for the reactor temperature profile

$$T = T^0 - \frac{n_A^0 \Delta_r H k}{C_p (\beta - k)} (\exp^{-kt} - \exp^{-\beta t}) \quad (14)$$

where

$$\beta = \frac{UA}{C_p} \quad (15)$$

If the initial condition is that the initial reactor temperature is T_i the following equation is obtained for the reactor temperature profile

$$T = T^0 - \frac{n_A^0 \Delta_r H k}{C_p (\beta - k)} (\exp^{-kt} - \exp^{-\beta t}) + (T_i - T^0) \exp^{-\beta t} \quad (16)$$

The parameters to be fitted in Eq. (14) are k and $\Delta_r H$ while in Eq. (16) they are k , $\Delta_r H$ and T_i .

Experimental

The experiments have been carried out in a computer controlled calorimeter programmed and assembled from readily available components in our laboratory [12] and more recently this calorimeter has been combined with a small fibre-optic coupled ultraviolet-visible absorption spectrometer [13]. The reactor has a capacity of 0.4 L and temperature measurements are made with low time constant platinum resistance thermometers. A data acquisition rate of ten cycles per minute is used and in a typical experiment several hundred data points, reactor temperature or chemical heat flow are available for analysis. The global heat transfer coefficient and the heat capacity of the contents of the reactor are determined on-line before and after the reaction using a programmable power supply and a calibration heater located inside the reactor.

In the first type of experiment the reactor was filled with 0.2 L of distilled water and the chemical reaction was simulated by programming the power supply to deliver an exponentially decreasing electrical power to the calibration resistance. In the experiment described here the initial electrical power was 20.00 W and a decay constant of $1.00 \cdot 10^{-3} \text{ s}^{-1}$ was used. With the assumption that the initial quantity of reagent was 1 mol the enthalpy of reaction is $20.00 \text{ kJ mol}^{-1}$. Figure 1 shows (a) the temperature profile of the reactor and (b) the chemical heat flow for an experiment carried out with a jacket temperature of 25°C .

In the second and third type of experiment acetic anhydride (99% pure supplied by Aldrich) was used

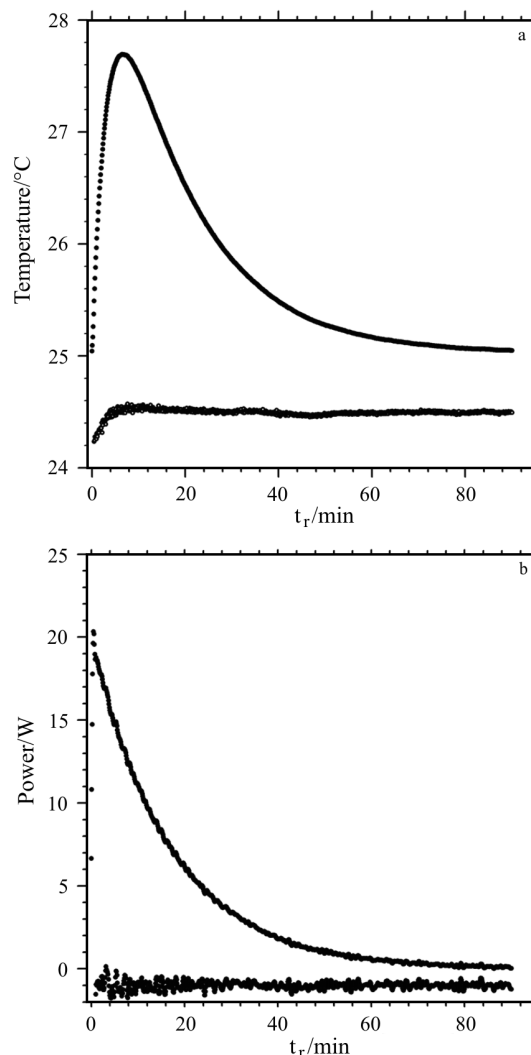


Fig. 1 To show the time variation of a – the reactor temperature and the residuals for the fit with $t_0=0.5$ min and b – the chemical heat flow and the residuals for the fit with $t_0=1$ min for the simulated reaction

and in the third type of experiment the other reagents used were methanol (99% pure supplied by Fluka) and concentrated sulphuric acid (98% pure supplied by Aldrich). In both types of experiment the acetic anhydride was weighed into a conical flask which was then placed in the thermostatic bath used to control the temperature of the jacket of the reactor. In the hydrolysis of acetic anhydride the reactor was filled with 12 mol of distilled water and the reaction was started by quickly adding 0.122 mol of acetic anhydride to the water. Figure 2 shows (a) the reactor temperature profile and (b) the chemical heat flow for a hydrolysis experiment carried out with the jacket temperature at 15°C . In the esterification experiment a solution of the desired quantity of sulphuric acid in methanol was placed in the reactor and the reaction was started by quickly adding the acetic anhydride.

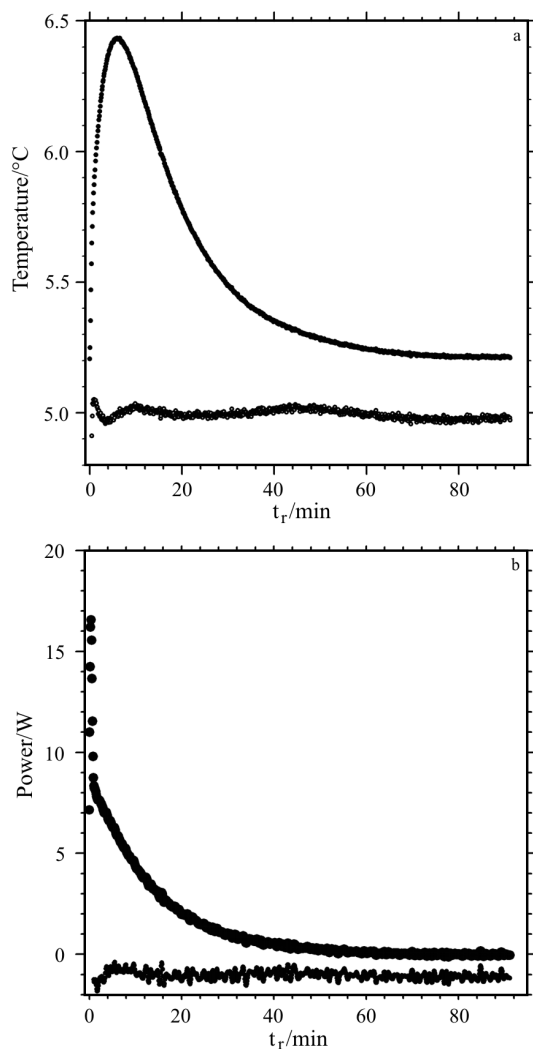


Fig. 2 To show the time variation of a – the reactor temperature and the residuals for the fit with $t_0=0.5$ min and b – the chemical heat flow and the residuals for the fit with $t_0=1$ min for the hydrolysis of acetic anhydride reaction

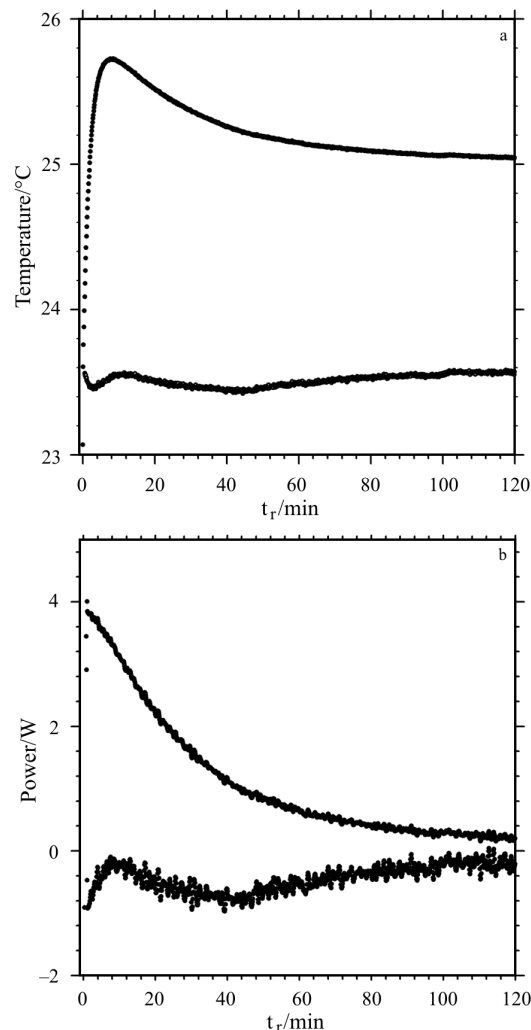


Fig. 3 To show the time variation of a – the reactor temperature and the residuals for the fit with $t_0=0.5$ min and b – the chemical heat flow and the residuals for the fit with $t_0=1$ min for the sulphuric acid catalysed esterification of acetic anhydride with methanol

Figure 3 shows (a) the reactor temperature profile and (b) the chemical heat flow for an experiment carried out with a jacket temperature of 25°C, 0.123 mol of acetic anhydride, 0.56 mmol of sulphuric acid and 6.0 mol of methanol.

Figure 1b shows that the chemical heat flow does not start with its maximum value. This can be attributed to the thermal inertia of the calibration heater. By contrast Fig. 2b shows a very high initial value of the chemical heat flow, this decreases very rapidly and then decays exponentially. The high initial value of the chemical heat flow and its rapid decrease may be attributed to an exothermic mixing of the reagents at 15°C. Figure 3a shows that the temperature inside the reactor decreases rapidly by $\sim 1.5^\circ\text{C}$ on mixing the reagents. This indicates that mixing the reagents is an endothermic process.

The data has been fitted using the Marquardt–Levenberg non-linear least squares method [14] as implemented in the Σ Plot graphics program [15]. In order to fit the data to Eqs (7), (14) or (16) it was necessary to prepare user defined equations using the Σ Plot transform language. The results of fitting the data are shown in Table 1 for the three reactions. For each fit Table 1 gives the coefficient of determination (r^2) and the standard error of the estimate ($\hat{\sigma}$) as well as the standard errors for the parameters which are quoted in parentheses in units of the least significant digit. Figures 1–3 also show the residuals (differences between the observed and calculated values of the dependent variable) for the best fits given in Table 1. For convenience the same axes have been used for the residuals and the dependent variables in Figs 1–3 and therefore the residuals have been multiplied by a factor of 3 and

Table 1 Comparison of the results of fitting the reactor temperature and the chemical heat flow for the three experiments

t_0/min	Eq. (14) or Eq. (16)				Eq. (7)					
	r^2	$\hat{\sigma}/^\circ\text{C}$	$T_f/^\circ\text{C}$	$10^3 \cdot k/\text{s}^{-1}$	$\Delta_r H/\text{kJ mol}^{-1}$	t_0/min	r^2	$\hat{\sigma}/\text{W}$	$10^3 \cdot k/\text{s}^{-1}$	$\Delta_r H/\text{kJ mol}^{-1}$
a										
0.0	0.9997	0.0132		0.975(1)	-20.28(1)	0	0.9865	0.560	0.956(6)	-20.29(9)
0.5	0.9998	0.0116		0.975(1)	-20.28(1)	1	0.9987	0.077	0.987(1)	-20.30(1)
b										
0.0	0.9987	0.0135	15.391(4)	1.253(3)	-61.06(8)	0	0.9579	0.470	1.37(2)	-60.8(5)
0.5	0.9998	0.0059	15.463(2)	1.234(1)	-60.85(3)	1	0.9987	0.071	1.222(2)	-60.82(8)
c										
0.0	0.9934	0.0187	23.460(6)	0.515(2)	-65.5(2)	0.5	0.9669	0.193	0.525(4)	-65.4(3)
0.5	0.9960	0.0142	23.510(6)	0.512(2)	-65.5(1)	1.0	0.9947	0.073	0.510(1)	-65.5(1)

translated in order to fit into the figures. In each case the residuals show small departures from being randomly distributed with respect to the reaction time.

Discussion

Table 1 shows that very similar values for the two parameters (k and $\Delta_r H$) are obtained by fitting the reactor temperature and the chemical heat flow. A significant improvement is obtained by eliminating some of the initial data from the fits. In fitting the reactor temperature it is necessary to remove less points to arrive at the optimum fit compared to fitting the chemical heat flow for the two chemical reactions but this is not so for the simulated reaction. In the first experiment the true values of the parameters are known and the fitting of both the reactor temperature and chemical heat flow gives estimated values of k and $\Delta_r H$ which differ by 1–2% from these. For the best fits these differences are considerably larger than the standard errors on the parameters. This indicates that the uncertainty in the parameters are determined by systematic rather than statistical errors. The most likely cause of a systematic error is a calibration error in the determination of the heat transfer coefficient and the heat capacity of the reactor contents. Changes of 1–2% in UA and C_p are sufficient to account for the differences between the real and fitted values of the parameters. The investigation of the effect of systematic errors is simpler for the fitting of the reactor temperature as it is only necessary to change the values of constants in the fitting code while in fitting the chemical heat flow it is necessary to recalculate this each time the constants are changed.

The value of the reaction rate constant for the hydrolysis experiment may be compared with that of $1.42 \cdot 10^{-3} \text{ s}^{-1}$ at 15°C reported by Gold [6] and the enthalpy of reaction may be compared with that of $-58.8 \text{ kJ mol}^{-1}$ calculated from the tabulated standard enthalpies of formation [16]. For the esterification reaction the enthalpy of reaction found here may be compared with that of $-66.8 \text{ kJ mol}^{-1}$ calculated from the standard enthalpies of formation [16].

When there is an enthalpy change on mixing the reagents this can be estimated as

$$\Delta_{\text{mix}} H = - \frac{C_p (T_i - T^0)}{n^0} \quad (17)$$

if the mixing is considered to occur adiabatically.

For the hydrolysis of acetic anhydride experiment a value of -4 kJ mol^{-1} is obtained and for the esterification experiment a value of 5 kJ mol^{-1} is obtained for the enthalpy of mixing. Using an estimated value of the heat capacity of acetic anhydride of

$230 \text{ J K}^{-1} \text{ mol}^{-1}$ [17] a simple heat balance calculation shows that for the hydrolysis experiment the initial temperature of the acetic anhydride would have to have been $\sim 25\text{--}30^\circ\text{C}$ in order to account for the adiabatic temperature rise of the reactor contents on the basis of a simple mixing of the reagents.

In conclusion it can be stated that fitting the reactor temperature and the chemical heat flow for quasi-isothermal reactions with pseudo-first order chemical kinetics carried out in an isoperibolic calorimeter give very similar results for the reaction rate constant and the enthalpy of reaction. Fitting the reactor temperature appears to have some advantages over fitting the chemical heat flow especially when both the enthalpy of mixing and reaction are exothermic.

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