A numerical study of the use of the Kissinger analysis of DSC thermograms to obtain reaction kinetic parameters

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Abstract

The analysis of DSC data to obtain reaction kinetic parameters is examined. The use of the Kissinger method to determine kinetic data is studied. It is demonstrated that it is not straightforward to distinguish single and multiple reactions using the Kissinger approach. Care must thus be taken in experimental design.

LIST OF SYMBOLS

A_i pre-exponential factor of the ith reaction
C_i concentration of reactant of ith reaction (mol m^{-3})
C_x concentration of compound x (mol m^{-3})
C_{0i} initial concentration of reactant of ith reaction (mol m^{-3})
C_0 initial concentration of reactant of first reaction (mol m^{-3})
E_{app} apparent activation energy $= -SR$ (kJ mol^{-1})
E_i activation energy of the ith reaction (kJ mol^{-1})
I Intercept of the line fitted to a Kissinger plot
ΔH_i heat of ith reaction (kJ mol^{-1})
δH difference between simulated and input heats of reaction (kJ mol^{-1})
I intercept of the line fitted to a Kissinger plot
n_i order of the ith reaction
R universal gas constant (kJ mol^{-1} K$^{-)}$
S slope of the line fitted to a Kissinger plot (K).
t time (s)
V volume of sample (m^3)
W power required (W)

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W_{mi} power required at ith maximum/minimum of DSC thermogram (W)

T_m temperature at peak of a DSC thermogram (K)

T_{mi} temperature at which ith maximum/minimum occurs (K)

δT Difference between simulated and analytical peak temperatures (K)

Greek letters

α scanning rate (K s^{-1})

β_1 A_2

β_2 E_1/R

β_3 E_2/R

β_4 $(E_1 + E_2)/R$

β_5 $A_1 E_1/R$

β_6 A_1^2

β_7 $(E_2 - E_1)/R$

β_8 $A_1 A_2 \Delta H_2/\Delta H_1$

β_9 $A_1 R/E_1$

β_{10} $(C_{01} \Delta H_1)^{-1}$

β_{11} A_1

INTRODUCTION

Differential scanning calorimetry (DSC) has often been used to calculate reaction kinetic parameters. Two techniques are commonly used in the literature. (i) In the Kissinger method, the variation of peak temperature with scanning rate and concentration is examined [1–3]. (ii) The Borchardt–Daniels method [4] utilizes the partial area under the thermogram to determine all of the reaction kinetic parameters (activation energy, pre-exponential factor, reaction order, and heat of reaction) from a single DSC run.

Although the Kissinger method requires data from several experiments in order to calculate reaction parameters, it has the advantage over the Borchardt–Daniels method of not relying on accurate knowledge of the position of the baseline of the thermogram; the temperature at which the maximum/minimum of the thermogram appears is usually obvious. The Borchardt–Daniels method is generally the one used by commercial software packaged with a DSC system.

Both the Kissinger and the Borchardt–Daniels methods assume a single reaction takes place during the scan. However, if more than one reaction is taking place, for example if the product of a decomposition reaction undergoes further decomposition, this assumption cannot be met. The Borchardt–Daniels method is not well suited to the analysis of multiple

reactions; kinetic parameters are obtained by least squares multiple regression of the DSC data. If multiple reactions are taking place the results will be nothing more than best fits to the data; different parameters will be obtained if different scanning rates and/or concentrations are used.

The Kissinger analysis is more likely to be able to detect and model multiple consecutive reactions. This paper examines the use of the Kissinger method in the study of such reactions with the aim of determining whether the method allows multiple reactions to be detected and their kinetic parameters quantified. Numerical simulations of DSC thermograms over a range of scanning rates, concentrations and kinetic parameters have been used in order to fulfil these aims.

ANALYTICAL SOLUTIONS FOR DSC

Analytical solutions for the temperature at which the maximum/minimum power occurs during DSC runs are useful in the mathematical modelling of the process, and in the determination of kinetic parameters.

Single reaction

Consider the single nth-order reaction $A \to B$, with heat of reaction ΔH. If the reaction kinetics show Arrhenius temperature dependence the reaction rate can be described by

$$\frac{dC_A}{dt} = -A \exp\left(-\frac{E}{RT}\right)C_A^n \tag{1}$$

DSC measures the change in rate of heat evolved or absorbed during an increase in temperature. The rate of heat evolved (W) at any particular time is proportional to the rate of the reaction, and can be described by eqn. (2).

$$W = V \Delta H A \exp\left(-\frac{E}{RT}\right)C_A^n \tag{2}$$

The temperature T_m at which the maximum deflection (i.e. $dW/dT = 0$) occurs is an easily recognized characteristic of a DSC thermogram. Differentiation of eqn. (2) with respect to temperature followed by manipulation yields eqn. (3) (the 'Kissinger plot').

$$\ln\left(\frac{\alpha}{T_m^2}\right) = \ln\left(\frac{ARC_0^{n-1}}{E}\right) - \frac{E}{RT_m} \tag{3}$$

Equation (3) describes the variation of peak temperature with scanning rate [1, 2] and holds for any single reaction of the form described occurring during DSC.

Equation (3) shows that a plot of $\ln(\alpha/T_m^2)$ against $1/T_m$ for a series of DSC thermograms using the same initial reactant concentration will have a slope $S = -E/R$ and an intercept $I = \ln(ARC_0^{n-1}/E)$; this is the basis of the Kissinger method. The activation energy of the reaction can then be calculated directly from a plot of eqn. (3). Note that the heat of the reaction can be calculated from the area under any of the thermograms ($\Delta H\, C_0\, V$). The intercept of the plot of eqn. (3) contains the product AC_0^{n-1}, so it is not possible to separate the reaction order from the reaction pre-exponential factor. It is thus necessary to carry out a further analysis step to determine the values of n and A separately. The slope and intercept of plots of eqn. (3) are functions of the protein concentration, as described by eqn. (4).

$$I + \ln(-S) = \ln A + (n - 1) \ln C_0 \tag{4}$$

A plot of $(I + \ln(-S))$ against $\ln C_0$ gives a straight line for any single reaction, no matter what its order. The slope of the line equals $(n - 1)$ and the intercept equals $\ln A$.

Using the extended Kissinger method (eqns. (3) and (4)) thus allows all of the reaction kinetic constants to be calculated from the peak temperatures of the DCS thermograms over a range of scanning rates and initial reactant concentrations.

Multiple consecutive reactions

Analysis of DSC peaks is considerably more complex for the case of multiple reactions.

Consider first two consecutive nth order reactions of the form

A → B   (reaction 1)
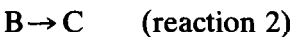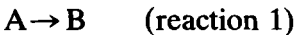
B → C   (reaction 2)

with enthalpies of reaction ΔH_1 and ΔH_2. If the reactions both follow Arrhenius kinetics, their rates can be written as

$$\text{Rate of reaction 1} = C_A^{n_1} A_1 \exp\left(-\frac{E_1}{RT}\right) \tag{5}$$

$$\text{Rate of reaction 2} = C_B^{n_2} A_2 \exp\left(-\frac{E_2}{RT}\right) \tag{6}$$

The rate of heat generation W is therefore

$W = V[(\text{rate of reaction 1})\Delta H_1 + (\text{rate of reaction 2})\Delta H_2]$

which can be rewritten in terms of eqns. (5) and (6) as

$$W = V\left[\Delta H_1\, C_A^{n_1} A_1 \exp\left(-\frac{E_1}{RT}\right) + \Delta H_2\, C_B^{n_2} A_2 \exp\left(-\frac{E_2}{RT}\right)\right] \tag{7}$$

There is no general analytical solution for $dW/dT = 0$ for eqns. (5)–(7). However, an analytical solution can be obtained for the special case of $n_1 = n_2 = 1$, i.e. when two consecutive first order reactions occur. This is given as eqn. (8), in which the various β terms (given in the List of symbols) incorporate the kinetic parameters. Equation (8), which holds for any maximum or minimum of the DSC thermogram, was first derived by Sandu and Singh [2].

$$\frac{\dfrac{\beta_1}{\alpha}\exp\left(\dfrac{\beta_2}{T_{mi}}\right) - \dfrac{\beta_3}{T_{mi}^2}\exp\left(\dfrac{\beta_4}{T_{mi}}\right)}{\dfrac{\beta_5}{T_{mi}^2}\exp\left(\dfrac{\beta_3}{T_{mi}}\right) - \dfrac{\beta_6}{\alpha}\exp\left(\dfrac{\beta_7}{T_{mi}}\right) + \dfrac{\beta_8}{\alpha}}$$

$$= \frac{\exp\left[-\beta_9\left(\dfrac{T_{mi}^2}{\alpha}\right)\exp\left(-\dfrac{\beta_2}{T_{mi}}\right)\right]}{\beta_{10}W_{mi} - \beta_{11}\exp\left\{-\left[\dfrac{\beta_2}{T_{mi}} + \beta_9\left(\dfrac{T_{mi}^2}{\alpha}\right)\exp\left(-\dfrac{\beta_2}{T_{mi}}\right)\right]\right\}} \qquad (8)$$

Here the constants β_8 and β_{10} differ slightly from those derived by Sandu and Singh [2]. These authors used an incorrect version of eqn. (7), in which the rate of change of the reaction intermediate (B) was used for the rate of the second reaction, rather than the rate of formation of the final product (C). In their derivation, β_8 and β_{10} contain $(\Delta H_2 - \Delta H_1)$ rather than the correct ΔH_1.

There is no general analytical solution for $dW/dT = 0$ when more than two consecutive reactions take place, or when two consecutive reactions are not both first order. To analyse reaction kinetics in real situations it is thus necessary to simulate the behaviour of the DSC rather than develop an analytical solution.

NUMERICAL SIMULATION

In this work, the numerical simulation of the thermograms resulting from the use of DSC on heat sensitive reactants has been achieved by solving eqns. (1) and (2) for the single reaction case, and eqns. (5)–(7) for the two reaction case. In addition, eqns. (9)–(12), for three consecutive reactions, have been simulated.

$A \xrightarrow{\Delta H_1} B \qquad$ (reaction 1)

$B \xrightarrow{\Delta H_2} C \qquad$ (reaction 2)
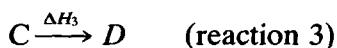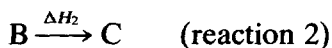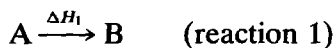
$C \xrightarrow{\Delta H_3} D \qquad$ (reaction 3)

$$\text{Rate of reaction } 1 = C_A^{n_1} A_1 \exp\left(-\frac{E_1}{RT}\right) \tag{9}$$

$$\text{Rate of reaction } 2 = C_B^{n_2} A_2 \exp\left(-\frac{E_2}{RT}\right) \tag{10}$$

$$\text{Rate of reaction } 3 = C_C^{n_3} A_3 \exp\left(-\frac{E_3}{RT}\right) \tag{11}$$
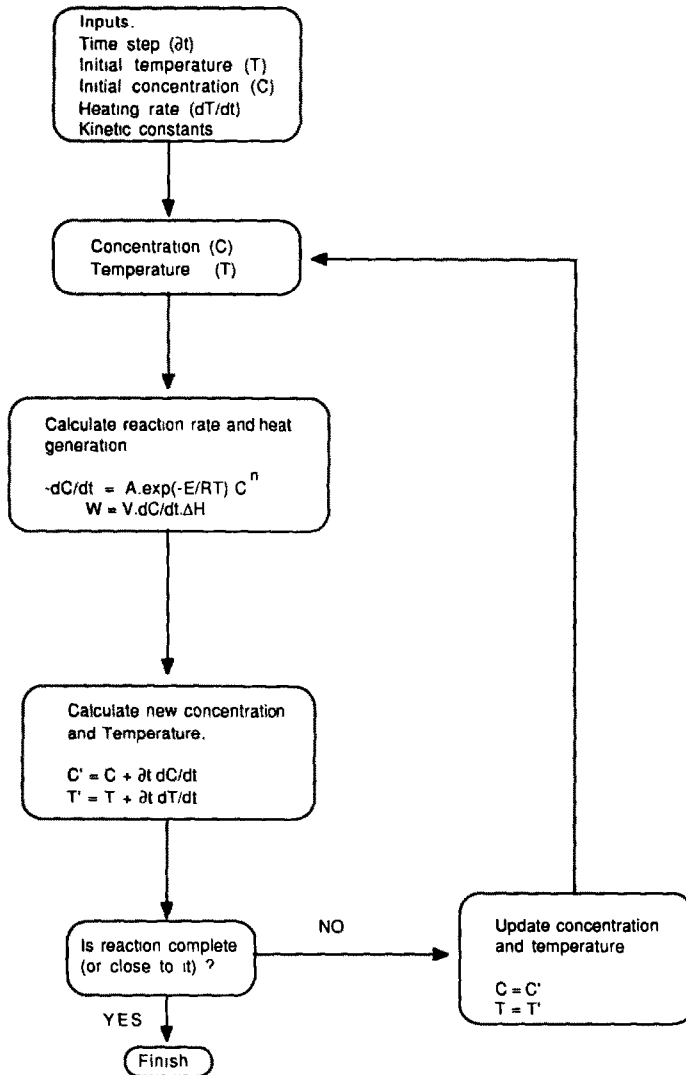

Fig. 1. Flow diagram of the numerical simulation of a DSC thermogram for a single reaction.

$$W = V\left[\Delta H_1 \, C_A^{n_1} A_1 \exp\left(-\frac{E_1}{RT}\right) + \Delta H_2 \, C_B^{n_2} A_2 \exp\left(-\frac{E_2}{RT}\right)\right.$$

$$\left. + \Delta H_3 \, C_C^{n_3} A_3 \exp\left(-\frac{E_3}{RT}\right)\right] \tag{12}$$

The calculations were carried out using FORTRAN programs run on a SUN workstation, but the programs are sufficiently simple that they could be run on any computer. A flow diagram of the program is given in Fig. 1. The program (i) calculates the rate of reaction, and hence the power required using given temperatures and concentrations for each component, (ii) calculates the change in concentration of each component at the end of a selected time interval, (iii) updates the conditions, then repeats the calculation steps until 99.999% of the reactant has been converted to the final product. With this method the choice of the time step δt is crucial to the accuracy of the simulations; this is discussed below.

Model testing

Single reaction model
The inherent accuracy of the model was first checked by running it with a single reaction and applying the following tests on the generated data. (i) The analytical solution for the variation of thermogram peak temperature with scanning rate (eqn. (3)) was used to predict peak temperatures. (ii) The total area under the DCS thermogram, equal to the total heat generated (or required) by the material was calculated. Division of the total area under the curve by the initial amount of material present ($C_0 V$) yields the heat of reaction.

Comparison of the calculated heat of reaction with that used to generate the simulation was used to test the overall accuracy of the calculations, while the simulated and analytical peak temperatures were compared to give a check of the intermediate calculations.

The time step used in the calculation is important both numerically and because the resolution of the calculated peak temperature depends on it: for example, if a scanning rate of 6 K min^{-1} and a time step of 1 s are used, the temperature steps are 0.1 K, making the resolution of the peak temperature 0.1 K.

Simulations were run for scanning rates between 0.25 and 20 K min^{-1} with a time step of 1 s for the thermal and kinetic parameters given in Table 1. Comparison between simulation and analytical results are also given in Table 1. The results show that the simulated peak temperature was within 0.001 K of the analytical result for a scan rate of 0.25 K min^{-1}, and the calculated heat of reaction was the same as the value input into the simulation. Accuracy decreased as scanning rate increased: at

TABLE 1

Comparison of constant time-step with constant temperature-step simulations for a single reaction with kinetic and scanning parameters of $C_0 = 10\ mol\ m^{-3}$, $\Delta H = 300\ kJ\ mol^{-1}$, $E = 200\ kJ\ mol^{-1}$, $n = 1$, $A = 10^{28}\ s^{-1}$, $T_0 = 20°C$; constant time step $= 1\ s$, constant temperature step $= 0.0042°C$

Scan rate $(K\ min^{-1})$	Analytical T_m (°C) (eqn. (3))	δT (°C) Constant time step	δT (°C) Constant temp. step	δH (J mol^{-1}) Constant time step	δH (J mol^{-1}) Constant temp. step
0.25	63.2868	−0.0007	−0.0007	0.000	0.000
0.75	68.3907	0.0032	−0.0010	0.001	0.000
1.00	69.7525	0.0025	−0.0017	0.001	0.000
1.50	71.6902	−0.0098	−0.0015	0.001	0.000
2.00	73.0782	0.0115	−0.0010	0.002	0.000
3.00	75.0532	0.0032	−0.0010	0.001	0.000
4.00	76.4680	0.0013	0.0013	0.001	0.000
5.00	77.5732	−0.0101	−0.0018	0.003	0.000
6.00	78.4814	−0.0186	−0.0019	0.007	0.000
8.00	79.9239	0.0572	−0.0011	0.009	0.000
10.00	81.0508	0.0508	0.0008	0.008	0.000
12.00	81.9769	−0.0231	0.0019	0.007	0.000
14.00	82.7635	−0.0032	0.0010	0.013	0.000
16.00	83.4478	−0.0189	0.0020	0.013	0.000
18.00	84.0535	−0.1465	−0.0007	0.004	0.000
20.00	84.5970	−0.0697	0.0012	0.020	0.000

$20\ K\ min^{-1}$ the simulated temperature was different by 0.07 K, and the heat of reaction was not as accurate as for $0.25\ K\ min^{-1}$.

Because temperature had the greatest effect on the reaction rate and the DSC signal, it was felt that it would be appropriate to keep the temperature step, rather than the time step, constant in calculations using different scanning rates. A temperature step of 0.0042 K was thus used in all calculations. Table 1 demonstrates that the simulation has a significantly better performance than the constant time step method: the peak temperatures were simulated to within the resolution of the method at the temperature step used (0.0042 K), whereas no difference between calculated and input heats of reaction could be found.

When the reaction order was increased from 1 to 2, the accuracy of the predictions was not as great: the calculated heat of reaction was still correct, but the peak temperatures were 0.11 K low (for a scanning rate of $0.25\ K\ min^{-1}$), and 0.13 K low (for a scanning rate of $20\ K\ min^{-1}$). The accuracy of the simulations were nevertheless considered sufficiently good to use a temperature step of 0.0042 K for all simulations, including those for multiple consecutive reactions.

Two consecutive reactions

Simulations were carried out for a wide range of conditions which could be predicted analytically using eqn. (8). Equation (8) contains two unknowns T_{mi} and W_{mi} and thus its solution for the peak temperature requires knowledge of the power at the peak. The maximum (or minimum) power calculated in the simulation was used in eqn. (8) to find the analytical peak temperature which was then compared with the simulated temperature. The simulated and analytical peak temperatures agree very well; the first peak temperature was simulated to within 0.2 K (and usually better) of the analytical solution, although the second peak temperature was generally less accurate.

The iterative method for the second peak was found to fail when the second reaction had an activation energy less than that of the first reaction by about $10 \, kJ \, mol^{-1}$, when the first reaction activation energy was $200 \, kJ \, mol^{-1}$. This emphasizes that even small differences in activation energy result in significant changes in reaction rate.

However, in practice the Kissinger method is usually applied to the first maximum/minimum of the thermogram; any subsidiary turning point is difficult to identify because the baseline of the DSC is not known. The accuracy of simulations using the two consecutive reaction model is thus considered sufficient for this investigation.

Conclusions about the model accuracies

The above tests indicated that the peak temperature of thermograms for single-reaction and two-reaction simulations has been predicted accurately. Although this has only been shown for a small number of special cases, it is felt that a similar accuracy can be assumed for any set of values for the reaction kinetic parameters. The accuracy of the predicted peak temperatures is sufficient to ensure that any analysis using the extended Kissinger method is also accurate, and represents what would be obtained from a series of experimental DSC runs with a chemical system having the same reaction kinetic parameters and scanning-rate/concentration combinations.

RESULTS OF NUMERICAL SIMULATIONS

Model predictions for single reactions

Simulations were carried out for DSC scanning rates between 0.25 and $20 \, K \, min^{-1}$, and for initial reactant concentrations between 2 and $20 \, mol \, m^{-3}$ for a wide range of values of the kinetic parameters (Table 2).

TABLE 2

The ranges of kinetic parameters studied in DSC simulations, together with the kinetic parameters used in the examples given

	Reaction order n	Activation energy E (kJ mol^{-1})	Pre-exponential factor A	Heat of reaction ΔH (kJ mol^{-1})
First reaction	0.5–4.0	50–400	10^{20}–10^{40}	−300 to +300
Second reaction	0.5–4.0	50–400	10^{20}–10^{40}	−300 to +300
Third reaction	0.5–4.0	50–400	10^{20}–10^{40}	−300 to +300
Kinetic parameters used to generate Figs. 2–4				
(a) First reaction	1	200	1×10^{28}	300
(b) Second reaction	2	210	5×10^{28}	−50
(c) Third reaction	1	190	5×10^{28}	−50

Table 2 also gives the kinetic parameters used in the examples given here. Figure 2 shows the Kissinger plot, and the extended Kissinger plot (plot of eqn. (4)) for the set of single reaction kinetics, line (a) in Table 2. The regression line to the data in Fig. 2(a) provides an example of the analysis of the data from a Kissinger plot. slope $= -24057$; i.e. $E = 8.314 \times 24057 = 200.010$ kJ mol^{-1} ($\delta E = 0.010$ kJ mol^{-1}). From the regression line in Fig. 2(b) and eqn. (4), it can be calculated that $n = 1.000$ and $A = 1.005 \times 10^{28}$.

For all the kinetic parameters tested here the Kissinger plots were linear ($r^2 > 0.99999$), demonstrating the accuracy of the theory and the stability of the program. The kinetic data retrieved from these plots, i.e. the values of the pre-exponential factor, the reaction order, and the activation energy of the reaction, were all in very good agreement with those used for the simulations: the pre-exponential factor was predicted to within 0.5%, while the activation energy and the reaction order were predicted with an accuracy of about 0.01%. The accuracy of the calculated pre-exponential factor is lower than the others because the value estimated by the extended Kissinger method is its logarithm.

These results demonstrate the power of the extended Kissinger analysis for determining the reaction kinetics of any single reaction taking place during DSC.

Model predictions for two and three consecutive reactions

It has been established that the simulation is accurate and that single reactions can be successfully modelled. However, we have been unable to
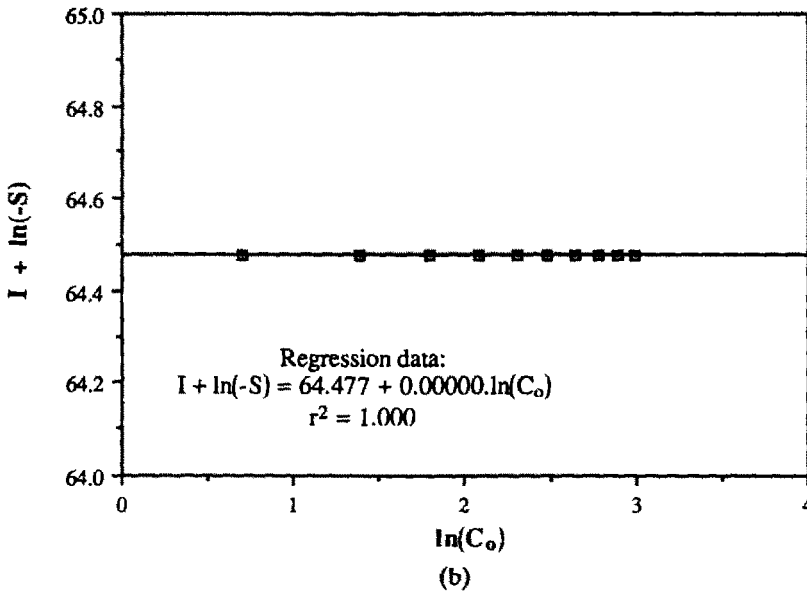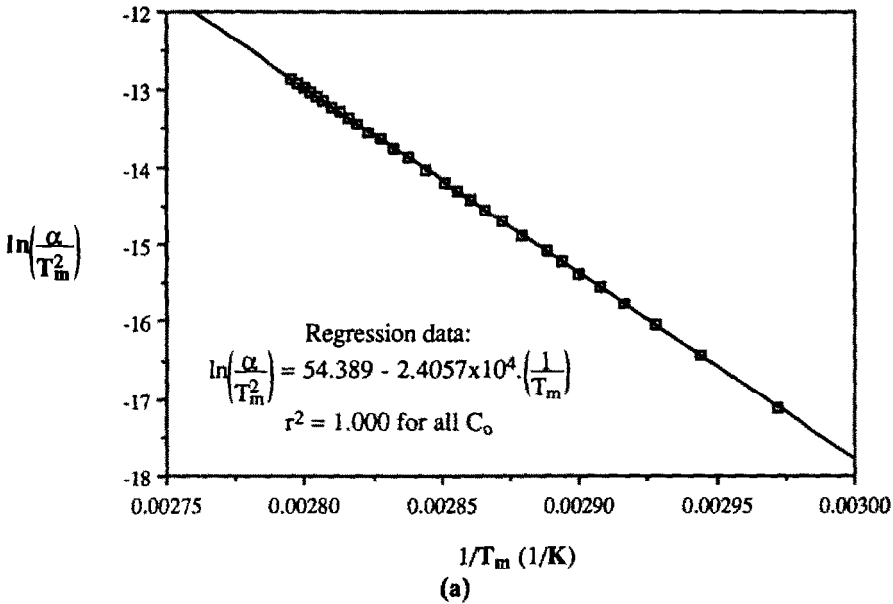
Fig. 2. Variation of peak temperature with scanning rate and concentration for a single reaction: (a) Kissinger plot of eqn. (3); (b) plot of eqn. (4). Reaction conditions given in line (a) of Table 2.

find reference to the use of the Kissinger method in situations where multiple consecutive reactions are known to be taking place, so the behaviour of the method under these conditions is uncertain.

Two limiting special cases were identified and successfully simulated for two consecutive reactions to confirm the accuracy of the programs.

(i) For very high activation energy of the second reaction ($E_1 =$ 200 kJ mol, $E_2 = 400$ kJ/mol, $A_1 \approx A_2$), the first reaction effectively goes to completion before the second reaction begins, so that the simulation is the same as a single reaction simulation up to the point where the second reaction becomes significant. The simulated thermograms using this reaction scheme are similar to that observed for β-lactoglobulin [5].

(ii) For very low activation energy of the second reaction ($E_1 =$ 200 kJ mol^{-1}, $E_2 = 100$ kJ mol^{-1}, $A_1 \approx A_2$), the second reaction takes place immediately any product of the first reaction is formed, so that $C_B \approx 0$. The results of the two-reaction simulation was thus a single reaction simulation with a reaction whose heat is equal to $\Delta H_1 + \Delta H_2$.

It is more difficult to study the case where both reactions occur within the same temperature range.

Model predictions for two and three consecutive reactions were carried out for a wide range of kinetic parameters (Table 2). Surprisingly, it was found that for all cases the Kissinger plots of $\ln(\alpha/T_m^2)$ vs. $1/T_m$ were straight lines, with $r^2 > 0.99999$, even though more than one reaction was taking place. It was thus not possible to detect a second (or third) reaction from the Kissinger plot. However, in contrast to the single reaction case, the plots of eqn. (4) were not linear: the shape was complex and dependent upon the particular combination of reaction kinetics used. Figures 3 and 4 show the plots of eqn. (4) for representative sets of kinetic parameters (given as lines (a)–(c) in Table 2) for two and three consecutive reaction simulations respectively; in each case the first reaction had the same kinetic parameters as that of the single reaction shown in Fig. 2. The lines of the Kissinger plot are straight to $r^2 \approx 1.000$. From the slope of the plot of $\ln(\alpha/T_m^2)$ vs. $1/T_m$ it is possible to find an apparent activation energy for the reaction, E_{app}. For the two-reaction example, E_{app} ranged from 199.553 to 200.750 kJ mol^{-1}; E_{app} ranged from 201.072 to 201.552 kJ mol^{-1} for the three-reaction example. E_{app} was thus a function of the initial reactant concentration. The order of the reaction and the pre-exponential factor are obtained by best-fit to the plots of eqn. (4): from Fig. 3(b), "n" $= 0.89031$ and "A" $= 1.697 \times 10^{28}$; from Fig. 4(b), "n" $= 1.14591$ and "A" $= 1.696 \times 10^{28}$. These lines are, however, very poor fits to what are obviously curves.

The fact that two and three consecutive reactions also produce straight lines when Kissinger plots are made of the peak temperature variation with scanning rate is important: a straight line Kissinger plot could be misinterpreted as being evidence that only one reaction is taking place. The apparent activation energy is an indeterminable combination of the activation energies of the consecutive reactions taking place and is, as shown above, different when different initial concentrations are used. The resulting "kinetic parameters" are as meaningless as the results of a
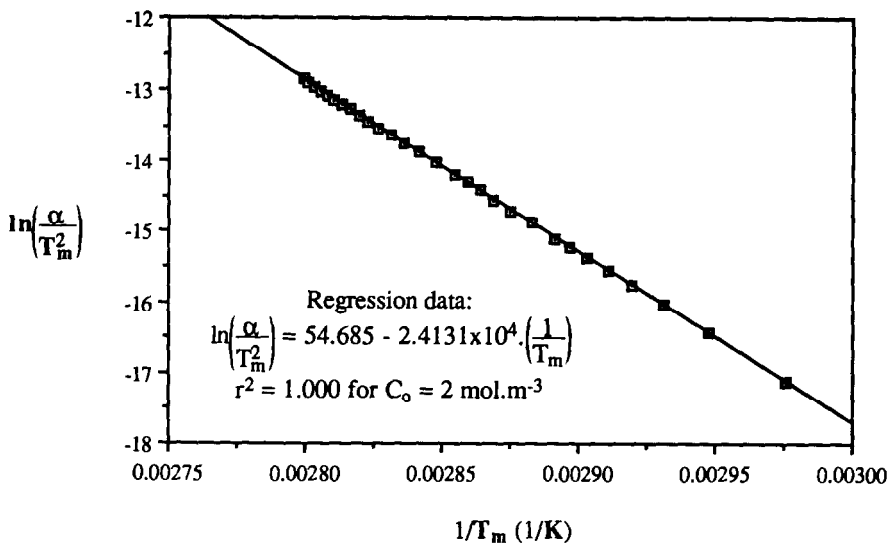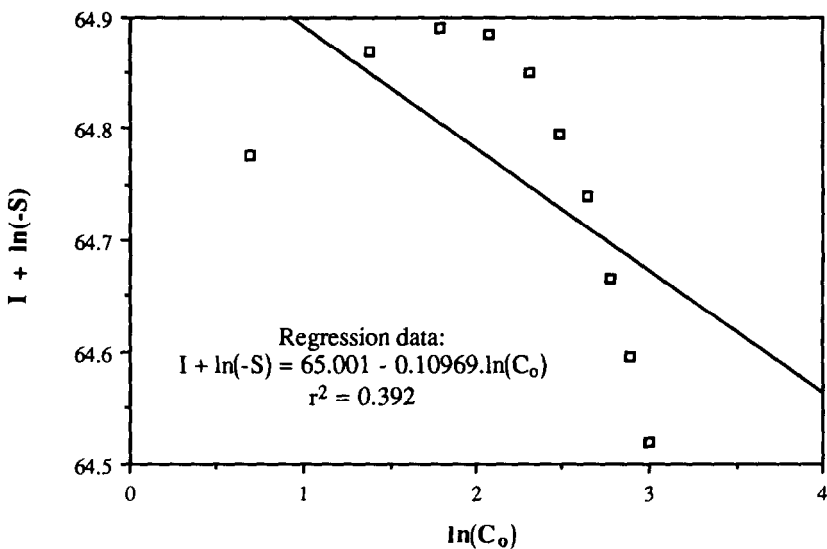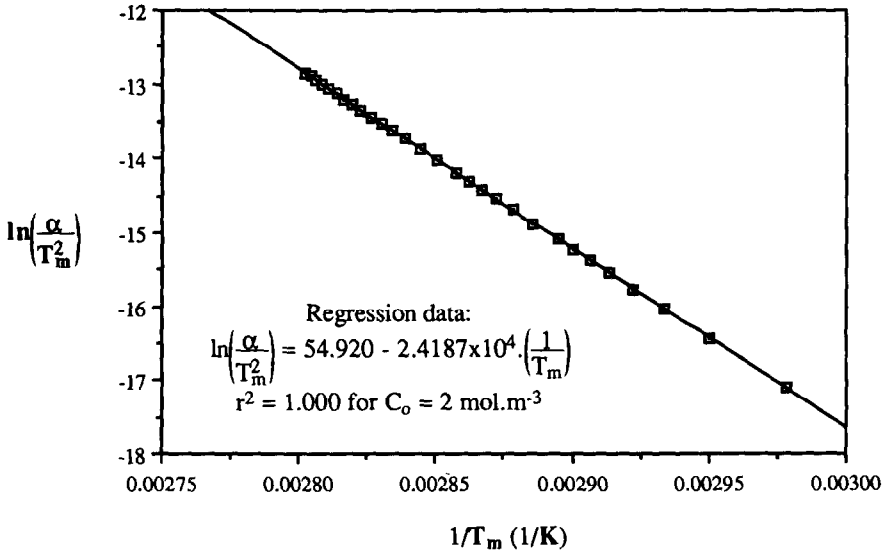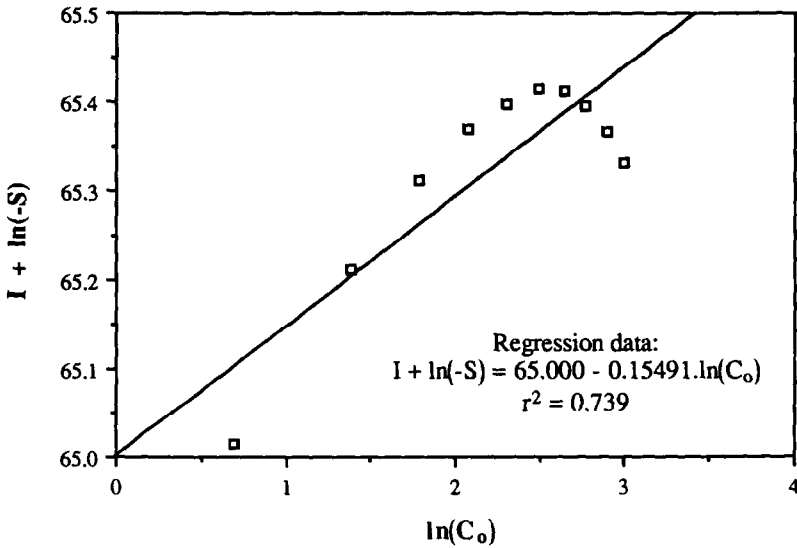
Fig. 3. Variation of peak temperature with scanning rate and concentration for two consecutive reactions: (a) Kissinger plot of eqn. (3); (b) plot of eqn. (4). Reaction conditions given in lines (a) and (b) of Table 2.

Borchardt–Daniels analysis of a DSC thermogram in the same situation. It may be that experimental error (e.g. the selection of incorrect baselines) could obscure the correct interpretation of data. Work is currently in progress to examine the effect of random error on the analysis of DSC. It is difficult to extract kinetic information regarding the two

(a)

(b)

Fig. 4. Variation of peak temperature with scanning rate and concentration for three consecutive reactions: (a) Kissinger plot of eqn. (3); (b) plot of eqn. (4). Reaction conditions given in lines (a), (b) and (c) of Table 2.

reactions from a Kissinger analysis; further work is needed to develop suitable numerical approaches. DSC thermograms should be carried out at a range of scanning rates and initial reactant concentrations: a non-linear plot of eqn. (4) demonstrates that more than a single reaction is taking place.

CONCLUSION

The simulations of single reactions taking place during DSC show that the use of the extended Kissinger method to analyse the thermograms produced at a range of initial concentrations and scanning rates is potentially a very accurate method for obtaining values for the reaction kinetic parameters. The Kissinger method is able to calculate values for the kinetic parameters with an error of less than 0.5% for the pre-exponential factor, and less than 0.01% for the reaction order and activation energy. The method is not able to recover estimates of the kinetic parameters from experimental DSC thermograms with this level of accuracy due to limitations in the accuracy of determining the peak temperature of the thermogram.

The numerical simulation of two and three consecutive reactions during DSC scans has shown that all Kissinger plots (eqn. (3)) are linear, regardless of the values of the kinetic parameters, whereas the extended Kissinger analysis yields plots that are non-linear. It is therefore important to carry out DSC scans at different initial reactant concentrations to avoid misinterpreting linear Kissinger plots as evidence of a single reaction taking place: the plot of eqn. (4) must also be linear for this to be the case. Experimental design and protocol must ensure that any kinetic parameters obtained by DSC adequately represent the reactions occurring. It has been shown that it is possible to confuse single and multiple reactions if great care is not taken.

ACKNOWLEDGEMENTS

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