

# D-optimal design of DSC experiments for $n$ th order kinetics

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**Abstract** D-optimal experimental designs are developed for differential scanning calorimetry experiments conducted under non-isothermal, constant heating modes under the assumption that the kinetics can be described by an  $n$ th order model. Two separate cases are considered: single-scan experiments in which the entire rate of reaction versus temperature curve is available, albeit only at selected points, and multiple-scan experiments in which only the temperature at the maximum in the DSC curve is available but it is known at several heating rates. For the single-scan experiment, the D-optimal heating rate and critical extents of reaction where the data should be analyzed are determined. For the multiple-scan experiment the three D-optimal heating rates are determined. For both cases, a hypothetical example is given which illustrates the success and limitations of this approach.

**Keywords** Cure kinetics · Differential scanning calorimetry (DSC) · D-optimal design · Thermosets

## Introduction

Differential scanning calorimetry (DSC) is a well known thermal analysis technique used in fields including materials science, polymer science, food science, and pharmaceuticals to measure thermal transitions including phase changes, crystallization kinetics, exothermic reaction kinetics, and endothermic reaction kinetics, to name just a few. Our interest at the moment is specifically in DSC experiments used to determine the kinetics of exothermic reactions such as those observed in reaction during food processing and storage. Traditionally, there are two modes in which such a DSC experiment may be conducted: isothermal experiments and constant heating rate experiments. In isothermal experiments, the sample and an inert reference in a separate test cell are quickly heated to the desired experimental temperature and the difference in the input energy required to maintain this temperature as the sample undergoes a thermal event is measured. This technique has the advantage of easier data analysis than the constant heating rate experiment but it is limited by examining only a single temperature at a time; requiring several experiments if kinetic parameters such as the activation energy are to be estimated. In constant heating rate experiments, the sample and the reference are heated at the same rate and the difference in the input energy required to maintain this heating rate is measured. This technique has the advantage of subjecting the sample to a range of temperatures and potentially requiring less experimental time since it is possible to perform only a single scan. But it does present slightly more difficult data analysis. In fact, two data analysis techniques have been developed and popularized for constant heating rate DSC experiments: single-scan full spectrum analysis [1, 2] and multiple-scan peak-temperature analysis [3, 4]. Inherent in the following

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analyses is the assumption that the rate of reaction is proportional to the instantaneous energy given off, i.e. it is assumed that the heat of reaction is constant and that there is no loss of mass during the experiment. Comparisons of these techniques have recently been conducted [5, 6] and have shown that it is necessary to select the appropriate kinetic model for the results to be useful.

In the single-scan technique, the sample and reference are heated at a constant rate and the data recorded during the entire experiment is used in conjunction with numerical analysis to estimate the kinetic parameters of the reaction. Typically, it is assumed that the reaction can, for the sake of subsequent modeling but not to infer reaction mechanisms, be modeled as an  $n$ th order reaction [7–9] of the form

$$\frac{\partial \alpha}{\partial t} = k(1 - \alpha)^n \quad (1)$$

where  $\alpha$ ,  $t$ ,  $k$ , and  $n$  are the fractional extent of reaction (unitless), time (s), Arrhenius rate constant ( $\text{s}^{-1}$ ), and the order of the reaction (unitless), respectively. The Arrhenius rate constant is assumed to have the following temperature dependence

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (2)$$

where  $A$ ,  $E$ ,  $R$ , and  $T$  are the pre-exponential factor ( $\text{s}^{-1}$ ), activation energy ( $\text{J mol}^{-1}$ ), the gas constant ( $8.314 \text{ J mol}^{-1} \text{ }^\circ\text{K}^{-1}$ ), and the absolute temperature ( $^\circ\text{K}$ ), respectively. Given this formulation, it is the three parameters  $n$ ,  $A$ , and  $E$  that must be determined from the DSC experiment.

Since the output from the DSC experiment is proportional to the left hand side of Eq. (1), one technique for estimating the kinetic parameters is to use non-linear regression techniques [10]. This requires that the raw data from the experiment be integrated to provide an estimate of the extent of reaction at selected points so that the right hand side of Eq. (1) can be evaluated. This can be done by integrating the DSC response curve from an initial point before the reaction has begun up to an ending point at which the reaction has been completed. This area is used to normalize the area under the DSC response from the initial point to selected intermediate points to provide estimates of the extent of reaction. A multiple parameter optimization technique can then be used to provide the least squares estimates of the parameters by minimizing the sum-of-squares of the residuals between the experimental results and the response predicted by Eqs. (1), (2).

A second approach [2], once the data has been integrated to provide estimates of the extent of reaction at various temperatures as described above, is to use a linearized version of Eqs. (1), (2), viz.

$$\ln\left(\frac{\partial \alpha}{\partial t}\right) = \ln(A) + n \ln(1 - \alpha) - \frac{E}{RT} \quad (3)$$

in conjunction with linear regression techniques to estimate the model parameters.

For the multiple-scan DSC technique, several experiments are performed at different heating rates and the temperature at which the peak in the DSC output occurs, i.e. the point at which the rate of the reaction is a maximum, is recorded. These maximum-point data are then used to estimate the activation energy by determining the slope of a plot of the logarithm of the heating rate versus the reciprocal of the absolute temperature [4]. The pre-exponential factor can also be calculated, however, the order of reaction is assumed in this approach to be identically equal to one, i.e.  $n \equiv 1$ .

For both of these techniques, it still remains a question as to what are the best experimental conditions under which the greatest accuracy in estimating the kinetic parameters can be achieved. Specifically, for the single-scan experiments the heating rate and the extents of reaction at which the analysis should be conducted must be specified. Likewise, for the multiple-scan technique, the question of which heating rates should be used must be identified. To answer these questions, the concept of D-optimal experimental design can be used.

The D-optimal experimental design concept for non-linear models was first introduced in 1959 [11] with a specific illustration of two sequential chemical reactions. This work showed that D-optimal designs result in an experimental design in which the volume of the joint confidence interval for the parameter estimates is minimized. This is to say that D-optimal designs provide the best possible design in the sense that they provide for the smallest possible confidence intervals on the estimated model parameters. To use the D-optimal approach [12], the generalized model response is written as

$$\hat{y} = f(x_i, \beta) \quad (4)$$

where  $\hat{y}$ ,  $X_i$ , and  $\beta$  are the predicted response, the experimental conditions for the  $i$ -th experiment, and the model parameters, respectively. For single-scan DSC the response is the temperature at which a specified extent of reaction has occurred ( $\hat{y} = T_\alpha$ ) and the experimental conditions that must be determined are

$$x_i = (h, \alpha_i)^T \quad (5)$$

where  $h$  is the heating rate ( $^\circ\text{K s}^{-1}$ ) and the superscript  $T$  indicates the transpose. For multiple-scan DSC, the model response is the peak temperature ( $\hat{y} = T_\alpha$ ) and the experimental conditions to be determined are

$$x_i = (h_i) \quad (6)$$

The three component model parameter vector for both cases is given by

$$\beta = (n, A, E/R)^T \tag{7}$$

where a scaled activation energy has been used for convenience.

For the generalized response model, the information matrix is introduced

$$\mathbf{M} = \sum_{i=1}^N \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \boldsymbol{\beta}} \frac{\partial f^T(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \boldsymbol{\beta}} \tag{8}$$

where  $N$  is the total number of experiments conducted. The (j,k) component of the information matrix is given by

$$M_{jk} = \sum_{i=1}^N \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_j} \frac{\partial f(\mathbf{x}_i, \boldsymbol{\beta})}{\partial \beta_k} \tag{9}$$

It has been shown that the determinant of the information matrix inverse is proportional to the volume of the joint confidence interval of the parameter estimates [12]. Therefore, the D-optimal design is the one for which the  $\mathbf{x}_i$  values are chosen so that the determinant of the inverse of the information matrix is a minimum or, equivalently, the determinant of the information matrix itself is a maximum.

Prior research has included work related to that considered herein. Cuna and Oliviera [13] examined the case for first-order kinetics under the condition of linearly increasing temperature where the initial temperature, heating rates, and sampling times were the design parameters of concern. They showed that the lowest possible initial temperature should be used and that rapid heating rates (frequently higher than practically possible) combined with sampling at fractional conversions of approximately 0.19 and 0.70 should be used. Rodríguez-Aragón and López-Fidalgo [14] studied the case in which only the Arrhenius equation was used (i.e. no concentration dependent functionality was included) and temperature was the only independent factor considered. Under these conditions, one of the D-optimal temperatures was the maximum in the experimental space while the other depended on the value of the activation energy. Other non-isothermal non-linear D-optimal designs have been developed specifically for diffusion controlled mass transfer [15, 16], application of the Bigelow model [17], the Weibull model [18], the Michaelis–Menten kinetic function [19], and growth curves [20].

### D-optimal designs for single-scan DSC experiments

For single-scan DSC experiments at a constant heating rate, the model response  $T_x$  is determined by combining Eqs. 1, 2 and integrating the results after substitution of  $t = (T - T_0)/h$  where  $T_0$  and  $h$  are the initial temperature (°K) and

heating rate (°K s<sup>-1</sup>), respectively. The final implicit expression for  $T_x$  is given as

$$\int_{T_0}^{T_x} \exp\left(\frac{-E}{RT}\right) dT = \frac{h(1 - (1 - \alpha)^{1-n})}{A(1 - n)} \quad n \neq 1 \tag{10}$$

$$= -\frac{h}{A} \ln(1 - \alpha) \quad n = 1$$

The derivatives needed to form the information matrix are given, for  $n \neq 1$ , by

$$\frac{\partial T_x}{\partial n} = \left(\frac{h}{A}\right) \left(\frac{1 - (1 - \alpha)^n}{(1 - \alpha)^2} - \frac{\ln(1 - \alpha)}{(1 - \alpha)^n}\right) \exp\left(\frac{E}{RT_x}\right) \tag{11}$$

$$\frac{\partial T_x}{\partial A} = -\left(\frac{h(1 - (1 - \alpha)^n)}{A^2(1 - \alpha)^n}\right) \exp\left(\frac{E}{RT_x}\right) \tag{12}$$

$$\frac{\partial T_x}{\partial (E/R)} = \exp\left(\frac{E}{RT_x}\right) \left[ \int_{T_0}^{T_x} \frac{1}{T} \exp\left(\frac{-E}{RT}\right) dT \right] \tag{13}$$

and for  $n=1$  they are given by

$$\frac{\partial T_x}{\partial n} = 0 \tag{14}$$

$$\frac{\partial T_x}{\partial A} = \left(\frac{h}{A^2} \ln(1 - \alpha)\right) \exp\left(\frac{E}{RT_x}\right) \tag{15}$$

$$\frac{\partial T_x}{\partial (E/R)} = \exp\left(\frac{E}{RT_x}\right) \left[ \int_{T_0}^{T_x} \frac{1}{T} \exp\left(\frac{-E}{RT}\right) dT \right] \tag{16}$$

Since the problem becomes independent of  $n$  when  $n = 1$ , the remainder of this paper will look only at the case for which  $1 < n$ .

Having completed the required mathematics, the information matrix can be easily determined. The solution to Eq. 10 was found using Newton’s method with a stopping criteria of a less than 10<sup>-10</sup> change in the solution for an individual iteration while the integrals were evaluated numerically using a 101 point Simpson’s rule; both written in Visual Basic for Applications Excel® macros. The inverse of the information matrix, its determinant, and the multivariate optimization required to minimize the determinant of the information matrix inverse were found using routines (MINVERSE, MDETERM and SOLVER, respectively) provided with Excel®. And, due to the difference in magnitude of the parameters, the logarithms of the pre-exponential factor and the scaled activation energy were used as the variables in the multivariate optimization.

Prior to any initial studies, it was necessary to define the range of the experimental parameters and the model parameters. The following experimental parameters were

used based on practical considerations while the model parameters were selected to encompass the wide range of values that might typically be seen in the food science arena:

$$1 \leq h(^{\circ}\text{K min}^{-1}) \leq 10 \quad (17)$$

$$0.10 \leq \alpha_i \leq 0.90 \quad (18)$$

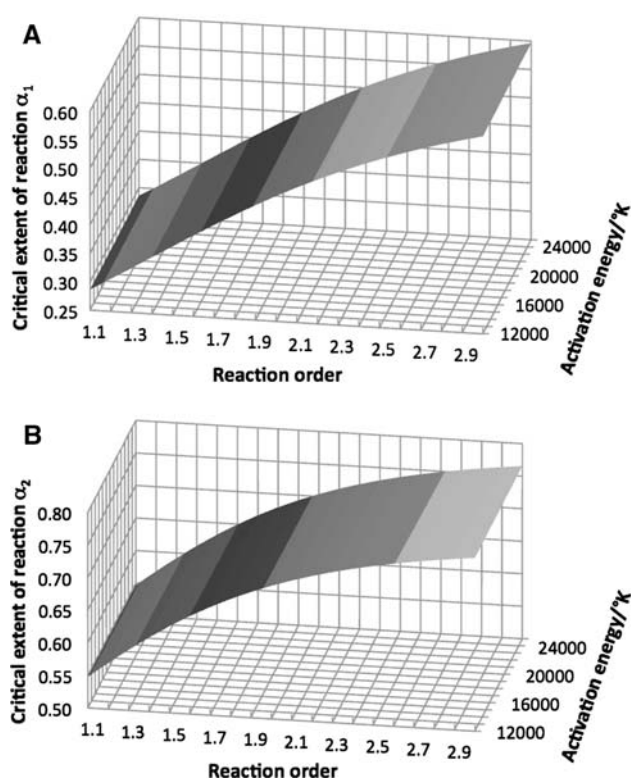
$$1 < n \leq 3 \quad (19)$$

$$10^{10} \leq A(\text{s}^{-1}) \leq 10^{20} \quad (20)$$

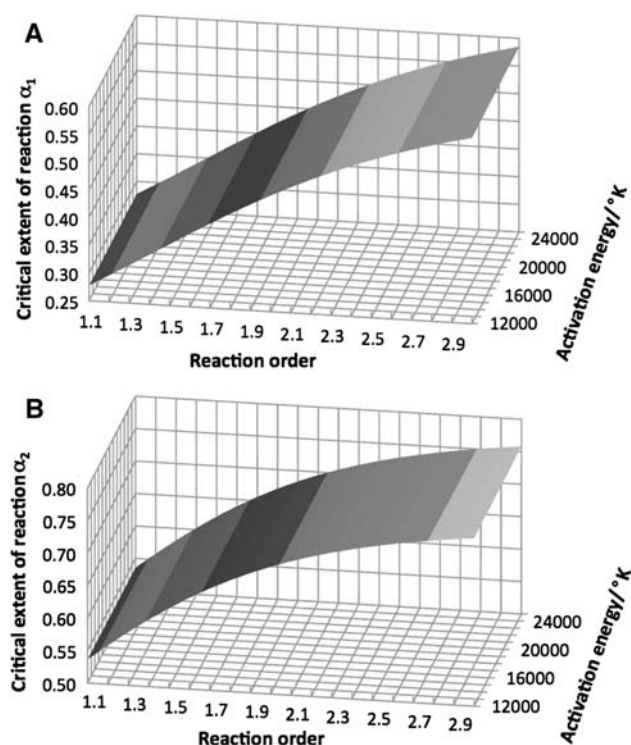
$$12000 \leq E/R(^{\circ}\text{K}) \leq 25000 \quad (21)$$

For D-optimal designs such as those considered here, the number of unique experimental conditions needed, i.e. the design points, corresponds to the number of parameters to be estimated [13]. More accurate estimates of the parameters are obtained by replicating these points; not by adding additional design points. Since the current application will estimate three parameters, three design points are required. Thus, for the single-scan DSC experiment the D-optimal heating rate and three extents of reaction, which will be referred to as the critical extents of reaction, must be determined. Extensive preliminary modeling over the range of parameters given in Eqs. 19–21 indicated that the D-optimal heating rate for all conditions was  $h = 10^{\circ}\text{K min}^{-1}$  and that the critical extents of reaction were  $0.10 \leq \alpha_1 < \alpha_2 < \alpha_3 = 0.90$ . Again, this is in keeping with D-optimal theory in which one of the design points is at the maximum of the design space [13]. This also had the effect of reducing the multivariate optimization from a 4-factor to a 2-factor problem. The preliminary work also indicated that it was necessary to use a very low initial temperature,  $T_0 = 233^{\circ}\text{K}$ , to achieve convergence for all combinations of the kinetic parameters. This was necessary since some combinations, especially large pre-exponential factors with low activation energies, resulted in reactions which were extremely rapid at or near the initial temperature and which seemed to require special attention. Another way to view this is that it was necessary for the experiment to begin approximately  $10^{\circ}\text{K}$  or more below the temperature at which noticeable reaction took place. This low initial temperature did not affect the results for reactions which began approximately  $10^{\circ}\text{K}$  or more above the initial temperature.

The second step in this study was to examine the effect of the kinetic parameters on the critical extents of reaction. Shown in Figs. 1, 2 and 3 are contour plots of  $\alpha_1$  and  $\alpha_2$  for  $\beta = (n, 10^{10}, E/R)^{\text{T}}$ ,  $\beta = (n, 10^{15}, E/R)^{\text{T}}$ , and  $\beta = (n, 10^{20}, E/R)^{\text{T}}$ , respectively. From these figures, it is apparent that  $\alpha_1$  and  $\alpha_2$  are essentially independent of  $E/R$ , but increase as the order of reaction increases. This same data was used to examine the effect of  $A$  at  $E/R = 17,000^{\circ}\text{K}$ , which was exemplary of the behavior at all other values of the scaled activation energy. As shown in Fig. 4, the dependence of



**Fig. 1** Critical extents of reaction  $\alpha_1$  (top) and  $\alpha_2$  (bottom) for  $\beta = (n, 10^{10}, E/R)^{\text{T}}$  for single-scan DSC experiments



**Fig. 2** Critical extents of reaction  $\alpha_1$  (top) and  $\alpha_2$  (bottom) for  $\beta = (n, 10^{15}, E/R)^{\text{T}}$  for single-scan DSC experiments

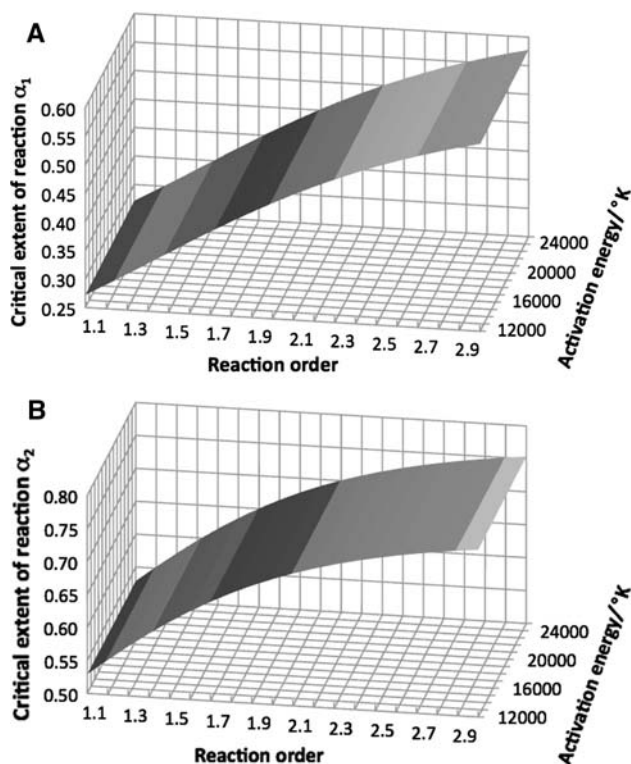


Fig. 3 Critical extents of reaction  $\alpha_1$  (top) and  $\alpha_2$  (bottom) for  $\beta = (n, 10^{20}, E/R)^T$  for single-scan DSC experiments

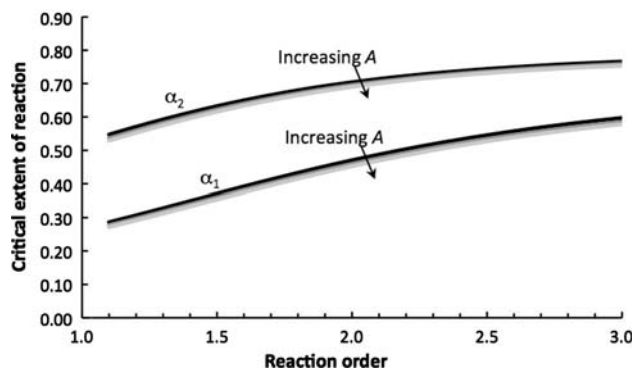


Fig. 4 Critical extents of reaction for  $\beta = (n, A, 17000)^T$  for single-scan DSC experiments

the critical extents of reaction on  $A$  is also very small and essentially indistinguishable at this scale. Based on this evidence, it was assumed for the remainder of the analysis that the critical extents of reaction were dependent only on the order of reaction. The data in Fig. 4 were correlated with the following expressions.

$$\alpha_1 = -0.0447 + 0.3335n - 0.041n^2 \tag{22}$$

$$\alpha_2 = 0.2177 + 0.3581n - 0.0598n^2 \tag{23}$$

The correlation coefficients for these two expressions were  $R^2 = 0.9996$  and  $R^2 = 0.9989$ , respectively. Further

applications of D-optimal designs for the single-scan case are considered later.

### D-optimal designs for multiple-scan DSC experiments

Multiple-scan DSC experiments require that the temperature at the peak in the DSC curve,  $T_p$ , be known since it is used to estimate the kinetic parameters. The expression for  $T_p$  can be found by differentiating Eq. 1 with respect to temperature while recalling that both  $k$  and  $\alpha$  are functions of temperature and then setting the resulting expression for  $(\partial^2 \alpha / \partial t \partial T)$  equal to zero. After simplification, the result is given as

$$0 = 1 - \left[ \frac{An}{h(E/R)} T_p^2 \exp\left(\frac{-E}{RT_p}\right) - \frac{A(1-n)}{h} \int_{T_0}^{T_p} \exp\left(\frac{-E}{RT}\right) dT \right] \tag{24}$$

From this expression the derivatives needed to form the information matrix are given by

$$\frac{\partial T_p}{\partial n} = \frac{1}{Z} \left[ \int_{T_0}^{T_p} \exp\left(\frac{-E}{RT}\right) dT - \frac{T_p^2}{E/R} \exp\left(\frac{-E}{RT_p}\right) \right] \tag{25}$$

$$\frac{\partial T_p}{\partial A} = -\frac{1}{AZ} \left[ \frac{nT_p^2}{E/R} \exp\left(\frac{-E}{RT_p}\right) + (1-n) \int_{T_0}^{T_p} \exp\left(\frac{-E}{RT}\right) dT \right] \tag{26}$$

$$\frac{\partial T_p}{\partial (E/R)} = \frac{1}{Z} \left[ n \left( 1 + \frac{T_p}{E/R} \right) \left( \frac{T_p}{E/R} \right) \exp\left(\frac{-E}{RT_p}\right) + (1-n) \int_{T_0}^{T_p} \frac{1}{T} \exp\left(\frac{-E}{RT}\right) dT \right] \tag{27}$$

with

$$Z = \left( 1 + \frac{2nT_p}{E/R} \right) \exp\left(\frac{-E}{RT_p}\right) \tag{28}$$

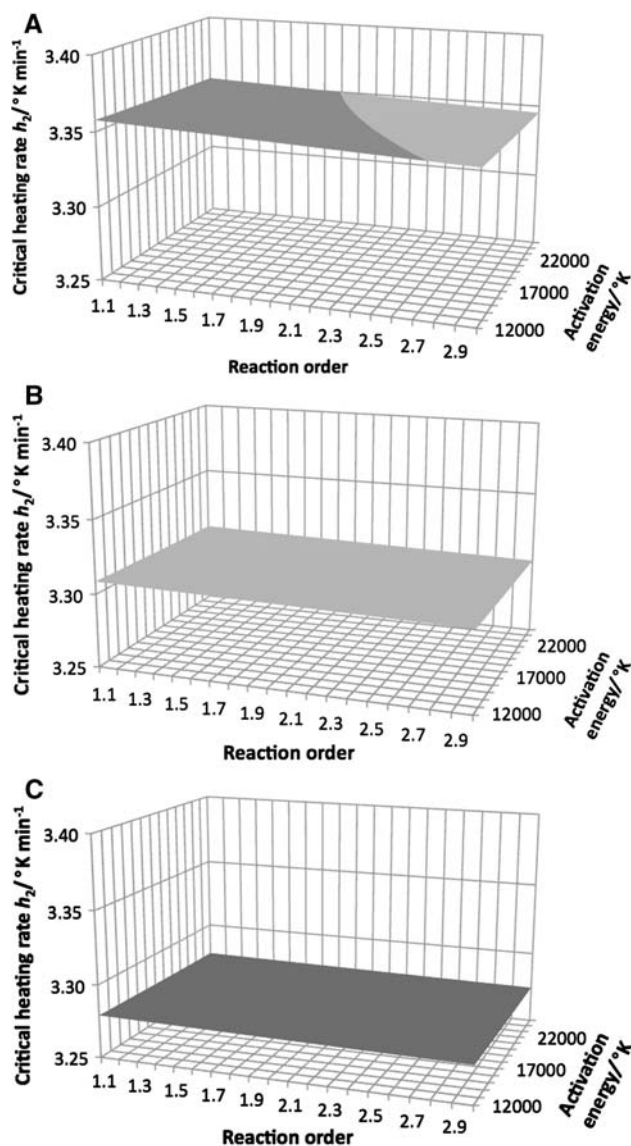
As with the single-scan design, three kinetic parameters are to be estimated and this requires three unique experimental design points. Again, extensive preliminary studies showed for the design parameters given in Eqs. 17–21 that the lowest possible and highest possible heating rates should be two of the three design points. This set  $h_1 = 1 \text{ }^\circ\text{K min}^{-1}$  and  $h_3 = 10 \text{ }^\circ\text{K min}^{-1}$  and reduced the optimization study to a single parameter,  $h_2$ . As shown in Fig. 5, the value of  $h_2$  was determined to be a function of all three kinetic parameters. However, for any given value

of the pre-exponential factor, it varied by less than 0.5% and so assuming it to be independent of the reaction order and activation energy introduces very little error. In fact, the original response surfaces which were determined numerically were so flat that finding stable answers accurate to four digits was practically impossible. Therefore, the results presented in Fig. 5 have been smoothed using a complete quadratic polynomial with the coefficients determined using linear least squares regression.

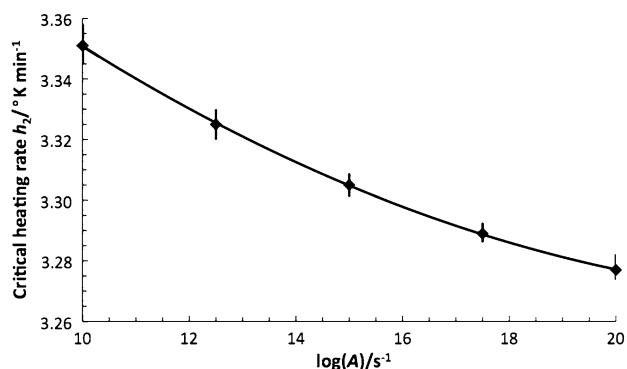
The dependence of  $h_2$  on the pre-exponential factor is shown in Table 1 where the average value and the range of the values are reported. These values were calculated for

**Table 1** Dependence of the critical heating rate  $h_2$  (K/min) on the pre-exponential factor,  $A$ , for multiple-run DSC experiments

Log(A)	$h_2$ ( $^{\circ}\text{K min}^{-1}$ )	
	Average	Range
10	3.351	0.013
12.5	3.325	0.009
15	3.305	0.007
17.5	3.289	0.005
20	3.277	0.005



**Fig. 5** Critical heating rate  $h_2$  for  $\beta = (n, 10^{10}, E/R)^T$  (top),  $\beta = (n, 10^{15}, E/R)^T$  (middle), and  $\beta = (n, 10^{20}, E/R)^T$  (bottom) for multiple-scan DSC experiments



**Fig. 6** Dependence of critical heating rate  $h_2$  on the pre-exponential factor for multiple-scan DSC experiments. The points represent the average response for  $\beta = (1 < n \leq 3, A, 11000 \leq E/R \leq 25000)^T$  while the vertical bars at each point represent the range of the data for the same kinetic parameter values. The solid curve represents the best fit quadratic polynomial

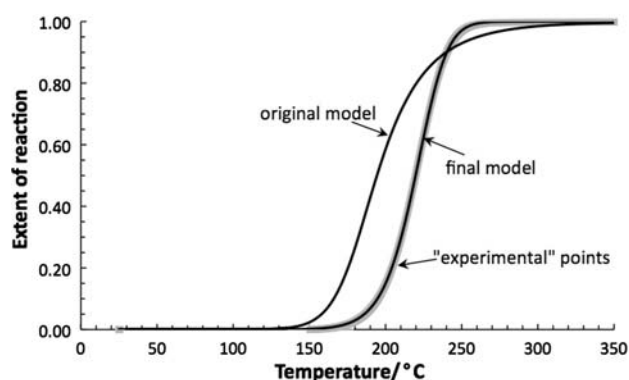
the ranges of reaction order and activation energy given in Eqs. 19 and 21. From the data in Table 1 it is apparent that there is a slight dependence on the pre-exponential factor which, as shown in Fig. 6, can be represented by

$$h_2 = 3.50 - 0.0183 \log(A) + 0.000366 * [\log(A)]^2 \quad (29)$$

The correlation coefficient for this approximation was  $R^2 = 0.9999$ . Further applications of D-optimal designs for the multiple-scan case are considered later.

**Applications of D-optimal designs**

Application of D-optimal designs can be studied using synthetic data created using the response model (with specified values of the kinetic parameters) and added random error to simulate experimental noise. For the single-scan technique, a synthetic data set along with an initial curve-fit, based on the (incorrect) assumption that the kinetic parameters  $\beta = (3, 10^{15}, 17432)^T$ , is shown in Fig. 7. Based on the assumption that  $n = 3$ , the critical



**Fig. 7** Synthetic “experimental” DSC data (*gray points*), initial curve based on assumed values of the kinetic parameters  $\beta = (3.00, 10^{15}, 17432)^T$ , and the final model curve using the fitted parameters  $\beta = (1.34, 4.91 \times 10^{13}, 17266)^T$

extents of reaction are 0.585, 0.758, and 0.900, respectively. For the synthetic “experimental” data, the closest values to these were 0.579, 0.756, and 0.897 where the corresponding values of  $T_x$  were 223.0 °C, 231.0 °C, and 240.0 °C, respectively. Using these three points, the best estimate of the kinetic parameters using Eq. 10 were determined to be  $\beta = (1.49, 1.59 \times 10^{15}, 19,000)^T$ . Since the value of the reaction order changed in this iteration, new values of the critical extents of reaction were determined. The theoretical values were 0.339, 0.603 and 0.900 while the closest experimental values were 0.331, 0.602, and 0.897 where the corresponding values of  $T_x$  were 212.0 °C, 224.0 °C, and 240.0 °C, respectively. Using these values to again estimate the kinetic parameters in Eq. 10 produced the estimate  $\beta = (1.34, 4.91 \times 10^{13}, 17,300)^T$ . A third iteration was conducted based on these values of the model parameters and with new values of the critical extents of reaction. The theoretical values for the critical extents of reaction were 0.329, 0.592 and 0.900 while the closest experimental values were 0.321, 0.590, and 0.897 where the corresponding values of  $T_x$  were 211.5 °C, 223.5 °C, and 240 °C, respectively. The resulting estimates of the model parameters at these conditions were unchanged to five digits and so these values were used as the final estimate. The values of the kinetic parameters used to generate the “experimental” data were  $\beta = (1.35, 2.6 \times 10^{13}, 17500)^T$ . Using this iterative technique in conjunction with D-optimal design resulted in estimates of the kinetic parameters very close to the “true” values used to generate the “experimental” data (see Table 2) and, as shown in Fig. 7, an excellent approximation to the behavior of the data. Not shown in Fig. 7 are any of the intermediate models since the improvement in the quality of the fitted curve from the first iteration to the third was visually indistinguishable even though the pre-exponential factor changed by nearly 2 orders of

**Table 2** Convergence of the kinetic parameters using D-optimal design criteria for the example in Fig. 7

Iteration	$\alpha_1$	$\alpha_2$	$n$	$A$ ( $s^{-1}$ )	$(E/R)$ ( $^{\circ}K$ )
0			3.00	1.00E+15	17,432
1	0.585	0.758	1.49	1.59E+15	18,916
2	0.339	0.603	1.34	4.91E+13	17,266
3	0.329	0.592	1.34	4.91E+13	17,266
“True” values			1.35	2.60E+13	17,500

magnitude. This is a result of the high correlation between the pre-exponential factor and the activation energy, i.e. many combinations of these two parameters result in nearly identical curves. Indeed, it is this high degree of correlation that makes estimating the kinetic parameters from a single curve so difficult.

For multiple-scan DSC analysis, synthetic data was again prepared using specified values of the kinetic parameters and adding random noise to the calculated results. As with the previous example, the assumed values of the kinetic parameters were  $\beta = (3, 10^{15}, 17400)^T$  and so the value of  $h_2$  at which the “experiment” was conducted was  $h_2 = 3.3 \text{ }^{\circ}K \text{ min}^{-1}$  as calculated from Eq. 28. The three experimental  $T_p$  values, including randomly added “noise,” are given in Table 3. Using non-linear regression analysis to minimize the sum-of-squares of the residuals between the experimental values and the values predicted by Eq. 24 provided the following estimate of the kinetic parameters  $\beta = (2.93, 2.29 \times 10^{13}, 17500)^T$ . These values for the pre-exponential factor and the scaled activation energy agree well with the values used to generate the synthetic data, viz.  $\beta = (1.35, 2.6 \times 10^{13}, 17500)^T$ . However, the order of reaction remained essentially unchanged from its original estimated value. Although additional studies were conducted, none led to an accurate estimate of  $n$ . This is due to the fact that  $n$  has almost no effect on the peak temperature and mostly affects only the shape of the rate of reaction versus temperature curve once the reaction has passed its maximum rate. Indeed, the shape of this curve prior to the maximum rate of reaction is almost completely independent of the order of reaction. Therefore, to accurately estimate the order of reaction, data from past the peak should be used and the single-scan

**Table 3** Synthetic “experimental” data for the multiple-scan DSC illustration

$i$	$h_i$ ( $^{\circ}K \text{ min}^{-1}$ )	$T_p$ ( $^{\circ}K$ )
1	1	467.5
2	3.3	480.6
3	10	496.3

technique is more appropriate when the order of reaction must be estimated.

## Conclusions

This work has shown that D-optimal designs can be used to select the experimental design points for both single-scan and multiple-scan DSC experiments conducted in non-isothermal mode using a constant heating rate. For the case of single-scan experiments, the experimental design points included the highest possible heating rate and the largest possible extent of reaction that could be reasonably measured. The other two critical extents of reaction were shown to be dependent on the order of reaction but essentially independent of the pre-exponential factor and the activation energy. An iterative data analysis technique on synthetic experimental data illustrated that accurate estimates of the kinetic parameters even when relatively poor estimates were made prior to “experimentation” was possible.

For the multiple-scan approach, which used the temperature at the maximum in the rate of reaction versus temperature curve, two of the critical heating rates were the slowest and fastest possible with the experimental apparatus. The third critical heating rate was shown to be only a function of the pre-exponential factor but that over the range of parameters studied varied by approximately  $\pm 1\%$  and that an approximate value of  $3.3\text{ }^{\circ}\text{K min}^{-1}$  would be suitable for most experiments. Analysis of synthetic data illustrated that accurate estimates of the pre-exponential factor and the activation energy could be obtained using three scans but that the order of reaction could not be accurately estimated using this technique.

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