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An evaluation of the relationship between kinetic data collection of DTG curves and its corresponding *R*-square and activation energy values for kinetic plots

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Abstract

In this study the significance of data point collection on *R*-square values and activation energy values of resulting kinetic plots is explored. Several data collection sets were examined to observe this phenomena. These data sets were taken from DTG plots of benzophenone. Benzophenone undergoes a zero-order kinetics process as it evaporates. The maximum number of data points, which may be utilized to give an optimum *R*-square value of 0.9999, is established. This number is the optimum number of data points that should be collected to ensure a resulting linear kinetic plot. This is also the number of data points which will provide a more accurate activation energy value determination. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: DTG; *R*-square values; Benzophenone; Kinetics; Activation energy

1. Introduction

As an evaporation process takes place from a well-defined constant surface area, it would be appropriate to conclude that the process is a zero-order reaction [1]. When an evaporation process is being carried out on a TG instrument, a kinetic plot may be obtained by collecting data points of the DTG curve. Kinetic plots for zero-order processes have been constructed on a regular basis since the establishment of the Arrhenius equation. Nevertheless, very little attention has been paid on evaluating and improving the fit of the line that represents the slope of the plot.

Usually, the *R*-square value from the kinetic plot would be indicative of the linearity of the slope of the plot. *R*-square values are generally used to measure the goodness-of-fit of a line when applied to scatter plots. *R*-square values are also representative of the correlation between the two variables of interest [2]. However, it has been noted that the *R*-square value fails to account for any continuous and consistent positive and negative deviations that may exist in data collection. It also fails to take into consideration any systematic deviations that are visible to the naked eye upon inspection, and assumes that such deviations are of a random nature. This study intends to clarify, and perhaps rectify this myth by examining the effects of data point collection on *R*-square values.

The linearity of a kinetic plot also affects the calculated activation energy value from a kinetic plot. By establishing the optimum number of data points to be used for a kinetic plot to obtain an *R*-square value of 1, a more accurate activation energy value may also be determined.

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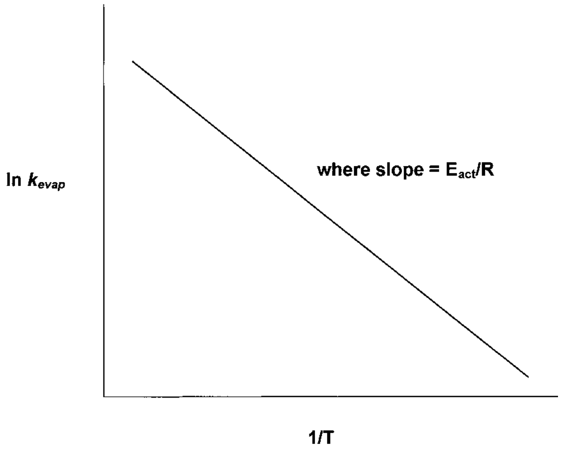

Fig. 1. A schematic diagram of a typical Arrhenius plot.

To obtain an Arrhenius plot, $\ln k_{\mathrm{evap}}$ values are plotted against inverse temperature, $1/T$ values (refer to Fig. 1 for a schematic diagram). This is based upon the Arrhenius equation, which is of the following form:

$$\ln k_{\mathrm{evap}} = \ln A_{\mathrm{evap}} - \frac{E_{\mathrm{act}}}{RT}$$

where k_{evap} is the coefficient of evaporation at a specified temperature, A_{evap} the corresponding pre-exponential factor, E_{act} the energy of activation, T the specific temperature at which the evaporation process takes place and R the gas constant value of 8.3145 J K^{-1} mol^{-1}. The k_{evap} values are read from the most linear portion of the slope of the DTG plots. The activation energy values were obtained by multiplying the slope of the kinetic plots by the gas constant. Since the activation energy value is dependent on the slope of the plot, the linearity of the plot will affect the accuracy of the determination of this value.

2. Materials and methods

In this study, the data from thermogravimetry studies of benzophenone were obtained with a TA simultaneous TG–DTA instrument, model number 2960. The benzophenone sample that was used for this study was acquired from Aldrich Chemicals. Platinum crucibles served as reference and sample cells. In order to determine the cross-sectional surface area of the sample cell, multiple inner-diameter measurements of the cell were taken. The sample was subjected to a rising temperature regime over the range of ambient to 400°C, at a heating rate of 2°C min^{-1}. It was investigated under dry compressed air, which flowed through the furnace chamber as a rate of 100 ml min^{-1}.

3. Results and discussion

Three sets of data points were read of the DTG curve for the sample. Five different cases were then established for these sets of data points. The first case consisted of 77 data points which were taken every 0.5°C min^{-1}. These data points were then plotted to get a kinetic plot (see Fig. 2). The corresponding R-square and activation energy values were obtained. This R-square value was 0.9994 and the calculated activation energy was 65.8 kJ. To observe the effects of the number of data points on R-square values, the number of data points were subsequently reduced in decrements of two data points per change. The reduction of points involved removing the first and last data points from each data sequence. This was done until two data points remained.

Logic tells us that when you draw a line between two points, you should always get an R-square value of 1 (refer to Fig. 3). This should be true as a line between two points which is perfectly linear. This indicates that if one intends to determine the optimum number of data points, this optimum number should have a value greater than 2, and it should also be the largest number of data points which may be incorporated to obtain a perfectly linear kinetic plot. From this data point manipulation exercise, it was determined that a range of 12 sets of data points may be used to acquire the optimum R-square value of 0.9999. The maximum number of points which may be used to get an optimum R-square value of 0.9999 is 39 data points. The resulting kinetic plot for this is shown in Fig. 4. The minimum number of data points required to give this optimum R-square value was 17 data points (see Fig. 5). The calculated activation energy values from both kinetic plots were 66.5 and 66.4 kJ, respectively. Table 1 displays all the R-square values and their corresponding activation energy values that are associated with the various data point sets.

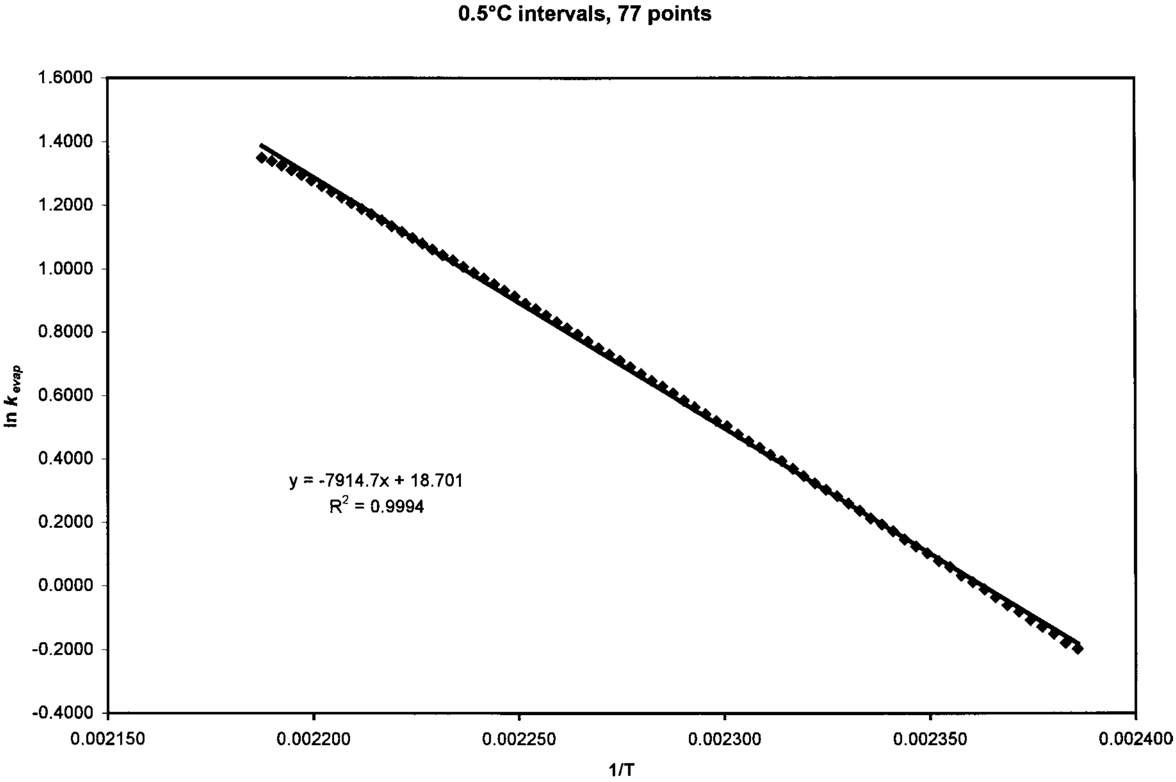

Fig. 2. An Arrhenius plot for benzophenone data taken at 0.5°C intervals, which includes 77 data points.

The second case consisted of 39 data points which were taken every 1°C min^{-1}. It should be noted that these data points were taken over the same range as studied in the previous case. These data points were also plotted to obtain an Arrhenius kinetic plot (see Fig. 6). The *R*-square value was 0.9994 and the calculated activation energy was 65.8 kJ for this case. As was done in case 1, the data points was once again reduced to determine the optimum number of data points that must be used to get the optimum *R*-square value. It is shown that six sets of data points provided this optimum *R*-square value. In this instance, a maximum of 19 data points may be used to obtain an *R*-square value of 0.9999 (see Fig. 7). This kinetic plot yielded a calculated activation energy value of 66.4 kJ. The minimum number of data points needed to obtain the same *R*-square value was nine data points (refer to Fig. 8). The calculated energy of activation was 66.7 kJ. The whole range of *R*-square values and their corresponding activation energy values that are associated with the various data point sets are tabulated as Table 2.

The function of the second case was to confirm the optimum *R*-square value was as stipulated by the previous case. The maximum number of points to be used for obtaining the desired *R*-square value was as expected, lesser than the previous case. This is in agreement with the conditions set by the data manipulation exercise as the starting number of data points used in the second case was smaller. In this case the effect of taking data points at a different interval was also observed, since data points were taken every 1°C min^{-1} instead of every 0.5°C min^{-1}.

In order to observe if data point intervals have an effect on the optimum *R*-square value for any given set of data points, a third case involving 20 data points taken at 2°C min^{-1} was studied (see Fig. 9). The same data point manipulation exercise was applied. In this case, only two sets of data points yielded the optimum *R*-square value of 0.9999 (see Figs. 10 and 11). These

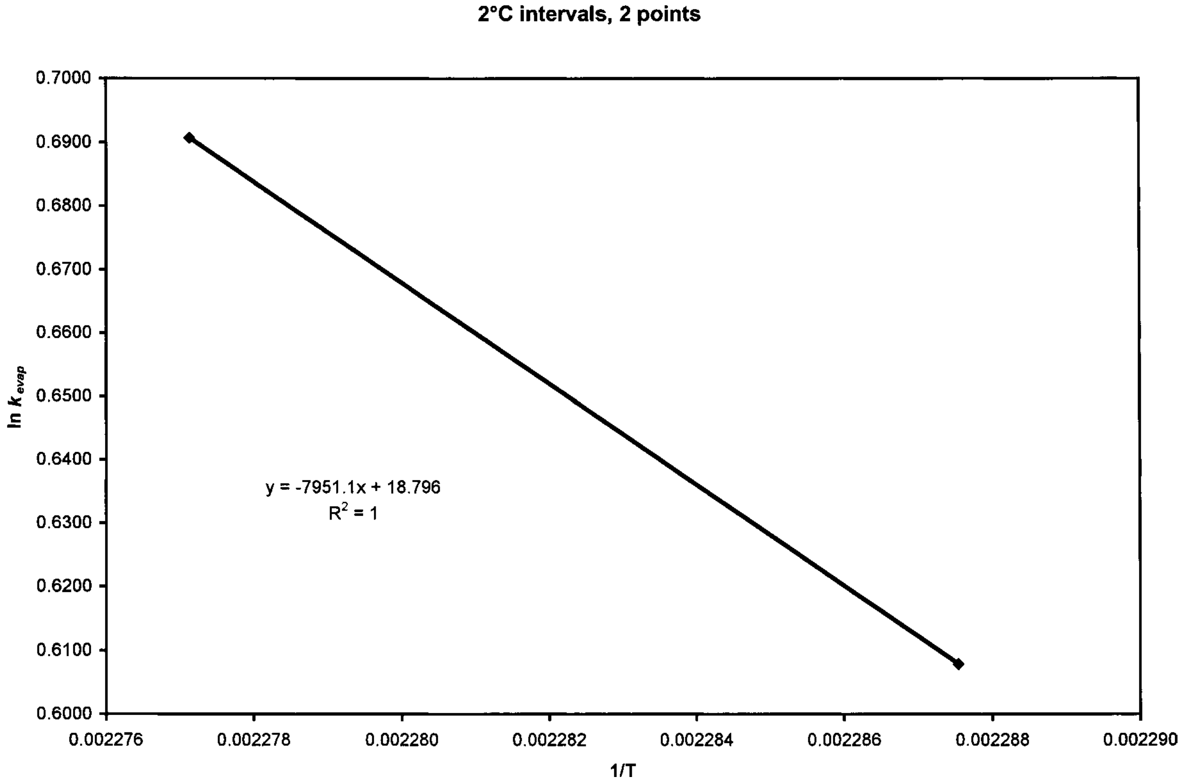

Fig. 3. An Arrhenius plot for benzophenone data taken at 2°C intervals, which includes two data points.

data sets had eight and six data points. The corresponding calculated activation energy values for both data sets were 66.7 kJ. Table 2 shows the whole range of *R*-square values and their corresponding activation energy values for all data sets. In this case, the number of data sets with the optimum *R*-square values was even smaller than that for cases 1 and 2. This result reinforces the hypothesis that data point interval has no significant effect on the overall linearity of the slope of kinetic plot if the right number of data points are employed.

In all three cases, it was observed that the *R*-square value fluctuates when different number of data points are used and that affects the calculation of activation energy values. It was also observed that in all cases, the activation energy values ranged from 66.5 to 66.7 kJ for the optimum *R*-square value of 0.9999. However, it should be noted that the second case was the best case studied as it employed a reasonable number of data points to obtain an acceptable *R*-square value and energy of activation value.

For the fourth case, data points taken at 1°C min^{-1} were re-examined. In this case these points were split into three separate regions (designated as start, middle and end) and plotted as three individual kinetic plots (see Figs. 12–14). From these three kinetic plots, values of activation energies were determined. These values were 68.2, 67.2 and 60.0 kJ, determined from Figs. 12–14, respectively. These values were compared with the activation energy values obtained from Figs. 6–8 (65.8, 66.4 and 66.7 kJ, respectively). It was observed that the value determined from Fig. 13 was closest to the values obtained from Figs. 7 and 8.

The *R*-square values from all three plots were also compared. The *R*-square values were 0.9997, 0.9999 and 0.9991 for each of the plots (refer to Figs. 12–14). By comparing the *R*-square values obtained from plotting all 39 data points (see case 2, Fig. 6) with the average *R*-square values from Figs. 12–14, it was observed that both values were comparable. This confirms that the supposed linearity determined by

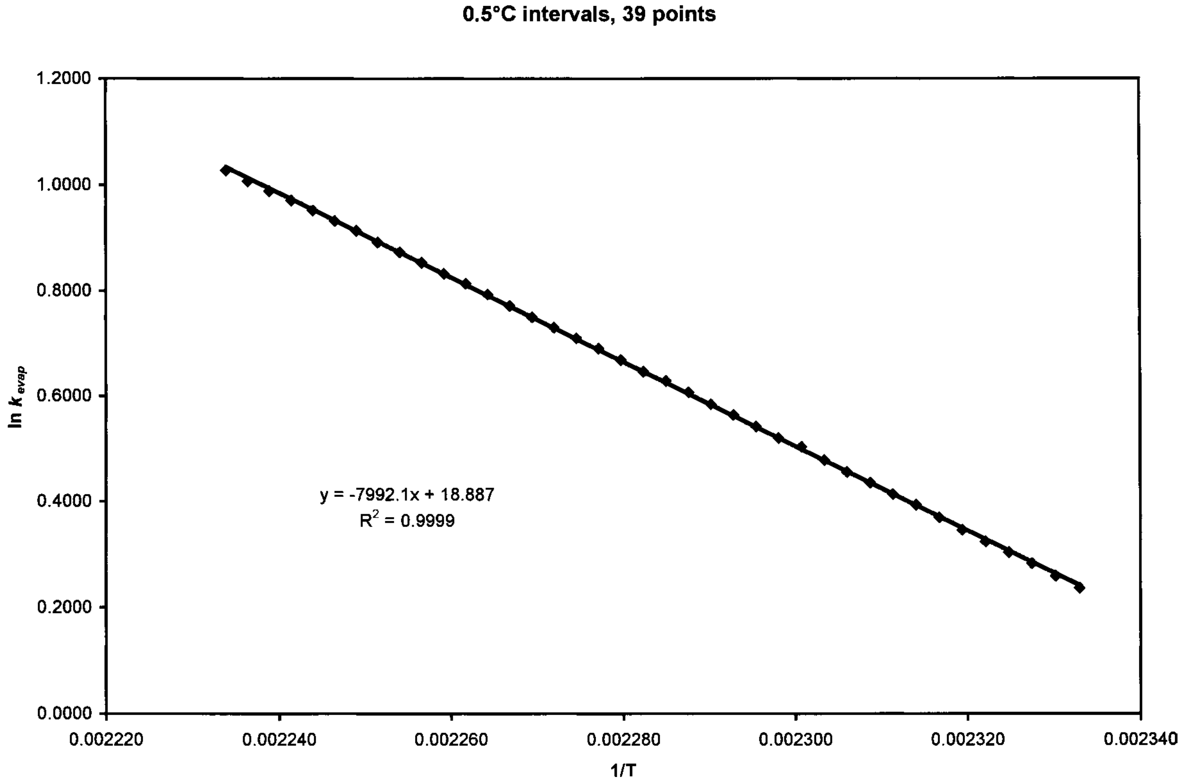

Fig. 4. An Arrhenius plot for benzophenone data taken at 0.5°C intervals, which includes 39 data points.

looking at the *R*-square values does not account for any curvatures in the kinetic plots.

Last but not least, in order to confirm the effects of curvatures in kinetic plots, a fifth case reminiscent of the fourth case was examined. In this case, 20 data points taken at intervals of 2°C $\min^{-1}$ were studied. As in case 4, the values were again split into three distinct regions and three kinetic plots were obtained (see Figs. 15–17). The activation energies determined from these plots were 68.3, 67.2 and 59.7 kJ, respectively. The *R*-square values for all three plots were 0.9998, 0.9999 and 0.9987, respectively. The result from this case study further advocates the hypothesis that the *R*-square value is not a good indication of the linearity of the slope, if the slope is consistently curvaceous and the summation of any positive and negative deviations are deflected.

For the last two cases that were studied, it should be mentioned that the original plots which included all data points (see Figs. 6 and 9) were divided into three distinct regions based upon α values calculated from TG data. These regions; the start, the middle and the end, correspond to the changes that occur within the sample as it is heated from ambient to the specified temperature. The start, or first portion of the original kinetic plot (see Figs. 12 and 15) coincides with the end of the reaction where the sample progressively diminishes. This occurrence indicates that the sample interface is no longer constant. The middle portion of the original kinetic plot (see Figs. 13 and 16) has the desired *R*-square value of 0.9999. These data points are taken of the most linear portion of the DTG curve. This is in agreement with the fact that the sample interface is constant during this period as the sample now exists in a liquid form. The final or end portion of the original kinetic plot (see Figs. 14 and 17) represents the reaction that is taking place at the onset of the experiment. This coincides with the initial evaporative process of the sample before it melts. By observing the conformity of the calculated α values with the

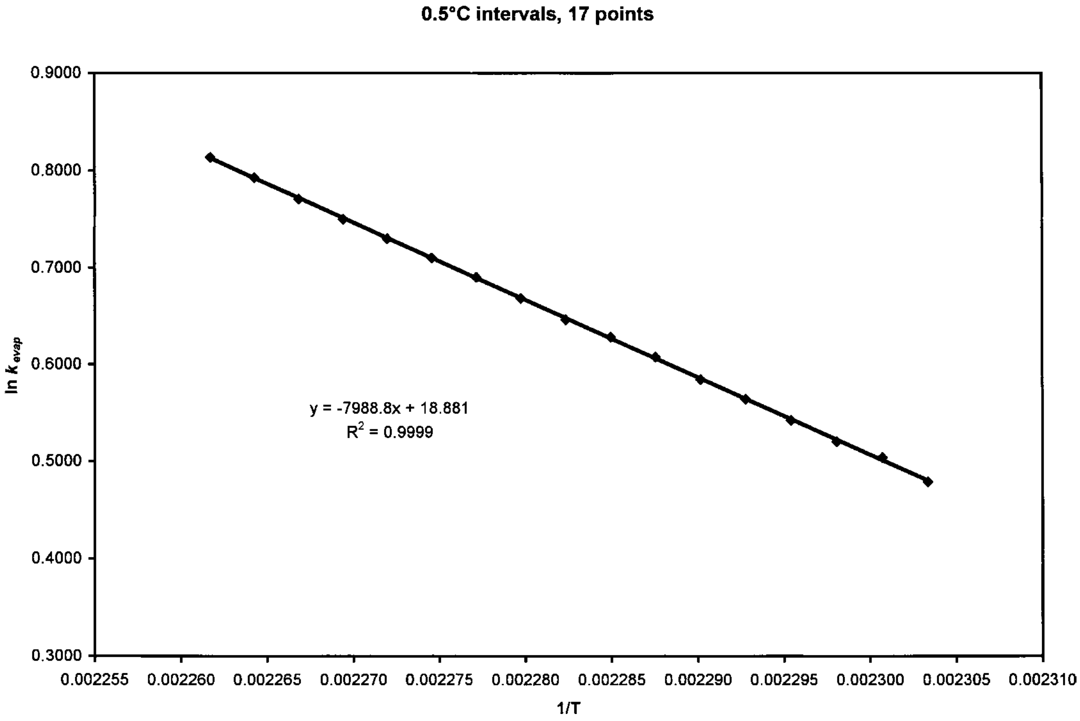

Fig. 5. An Arrhenius plot for benzophenone data taken at 0.5°C intervals, which includes 17 data points.

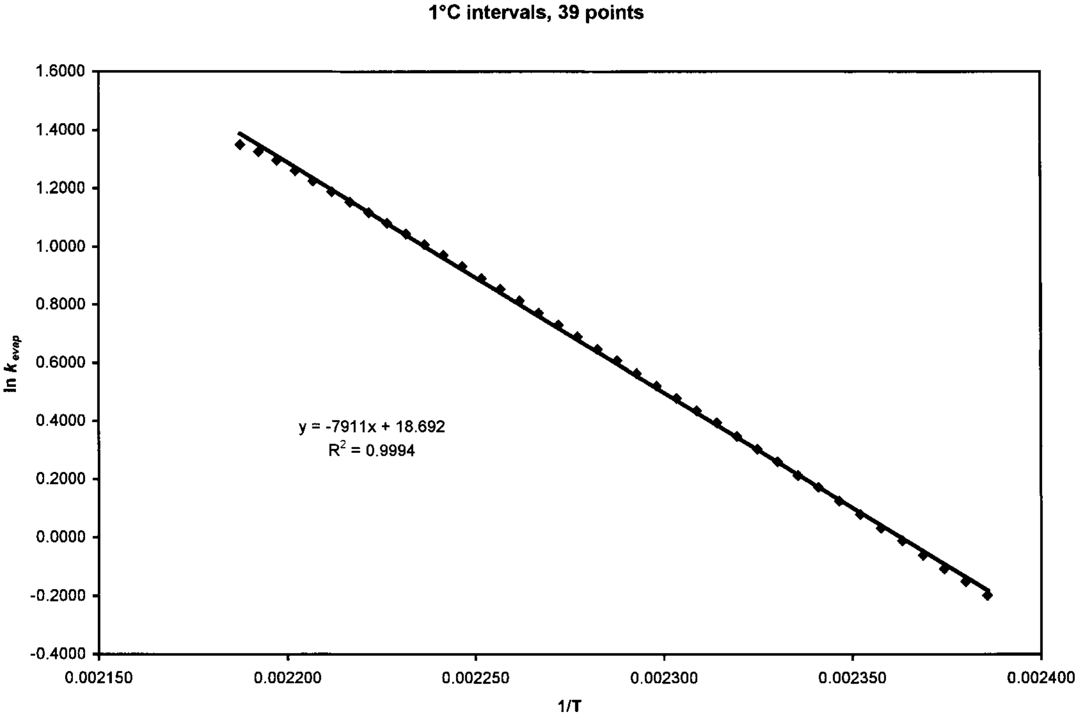

Fig. 6. An Arrhenius plot for benzophenone data taken at 1°C intervals, which includes 39 data points.

Table 1
The R-square values and calculated activation energy values for a benzophenone data set which was taken at 0.5°C intervals

Number of points	R-square value	E_{act} (kJ)
77	0.9994	65.8
75	0.9995	65.9
73	0.9995	65.9
71	0.9996	66.0
69	0.9996	66.0
67	0.9996	66.0
65	0.9996	66.0
63	0.9997	66.0
61	0.9997	66.1
59	0.9997	66.1
57	0.9997	66.1
55	0.9997	66.1
53	0.9997	66.2
51	0.9997	66.2
49	0.9998	66.2
47	0.9998	66.3
45	0.9998	66.3
43	0.9998	66.4
41	0.9998	66.4
39	0.9999	66.5
37	0.9999	66.5
35	0.9999	66.5
33	0.9999	66.5
31	0.9999	66.6
29	0.9999	66.5
27	0.9999	66.5
25	0.9999	66.5
23	0.9999	66.5
21	0.9999	66.5
19	0.9999	66.5
17	0.9999	66.4
15	0.9998	66.3
13	0.9998	66.5
11	0.9998	66.4
9	0.9997	66.4
7	0.9993	66.5
5	0.9986	65.6
3	0.9969	63.6

Table 2
The R-square values and calculated activation energies associated with the data point reduction manipulation exercise for a benzophenone data set which was taken at 1°C intervals

Number of points	R-square value	E_{act} (kJ)
39	0.9994	65.8
37	0.9995	65.9
35	0.9996	66.0
33	0.9996	66.0
31	0.9997	66.1
29	0.9997	66.1
27	0.9997	66.2
25	0.9998	66.2
23	0.9998	66.3
21	0.9998	66.4
19	0.9999	66.4
17	0.9999	66.5
15	0.9999	66.6
13	0.9999	66.5
11	0.9999	66.6
9	0.9999	66.7
7	0.9998	66.5
5	0.9997	66.2
3	0.9995	66.1
S	0.9997	68.1
M	0.9999	67.2
E	0.9991	60.0

systematic curves that are evident in each kinetic plot, the way in which the data points were divided into the three regions may be validated.

From all the cases that were studied, it may be concluded that there is a set of optimum data collection experimental conditions. In order to get a meaningful R-square value which indicates the true nature of the slope of any kinetic plots, it would be necessary to take data points at a recommended data point interval of 1°C between each data point. It was also observed that in many cases, the activation energies are affected by the linearity of these slopes since the determination of such values are dependent on the values of these slopes. To get precise activation energy values, it is advisable to either select the middle region of a kinetic plot or to determine this value based on the activation energy values calculated from three separate kinetic plots.

4. Conclusion

Based upon this study, it was concluded that there exists a set of optimum data collection conditions which provide a meaningful R-square value of 0.9999. However, the optimum number of data points that should be collected to ensure a resulting linear kinetic plot varies from a case to case basis, as demonstrated above. Although it has been shown that data point collection intervals have no significant effects on the overall linearity of the slope of kinetic plots when the right number of data points are

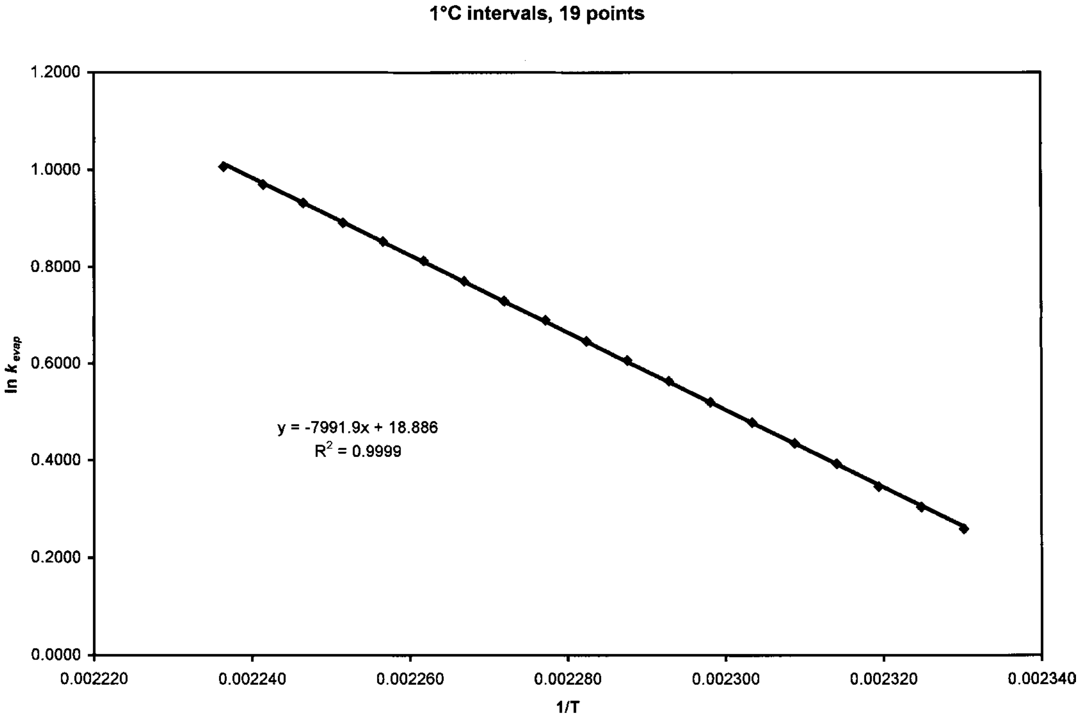

Fig. 7. An Arrhenius plot for benzophenone data taken at 1°C intervals, which includes 19 data points.

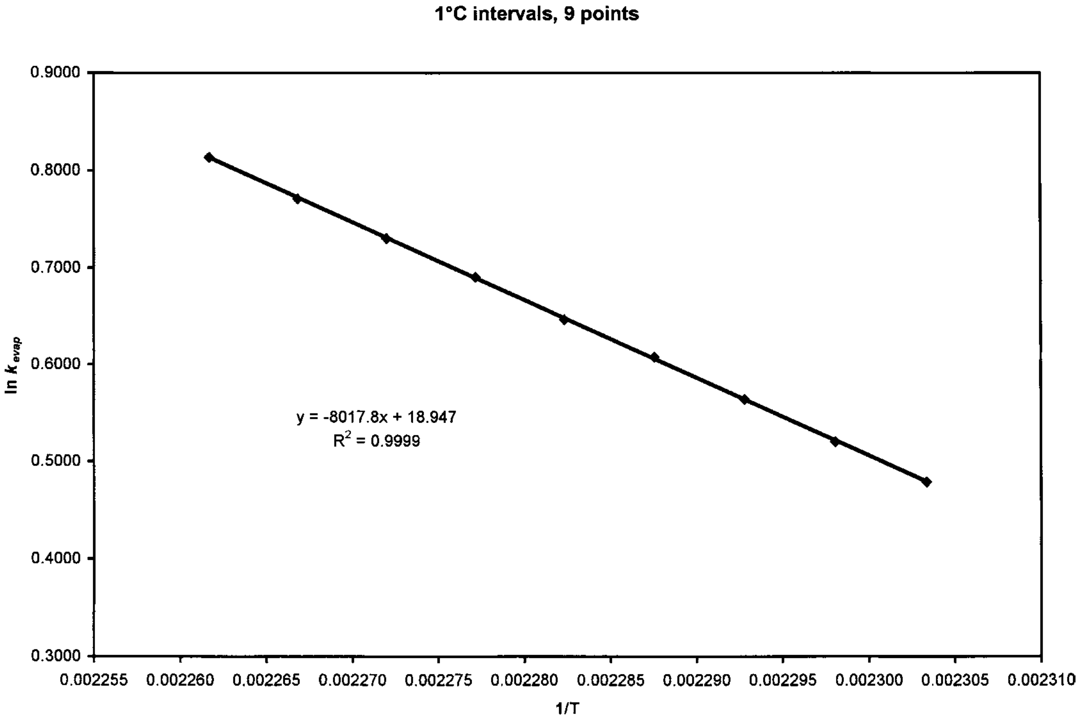

Fig. 8. An Arrhenius plot for benzophenone data taken at 1°C intervals, which includes nine data points.

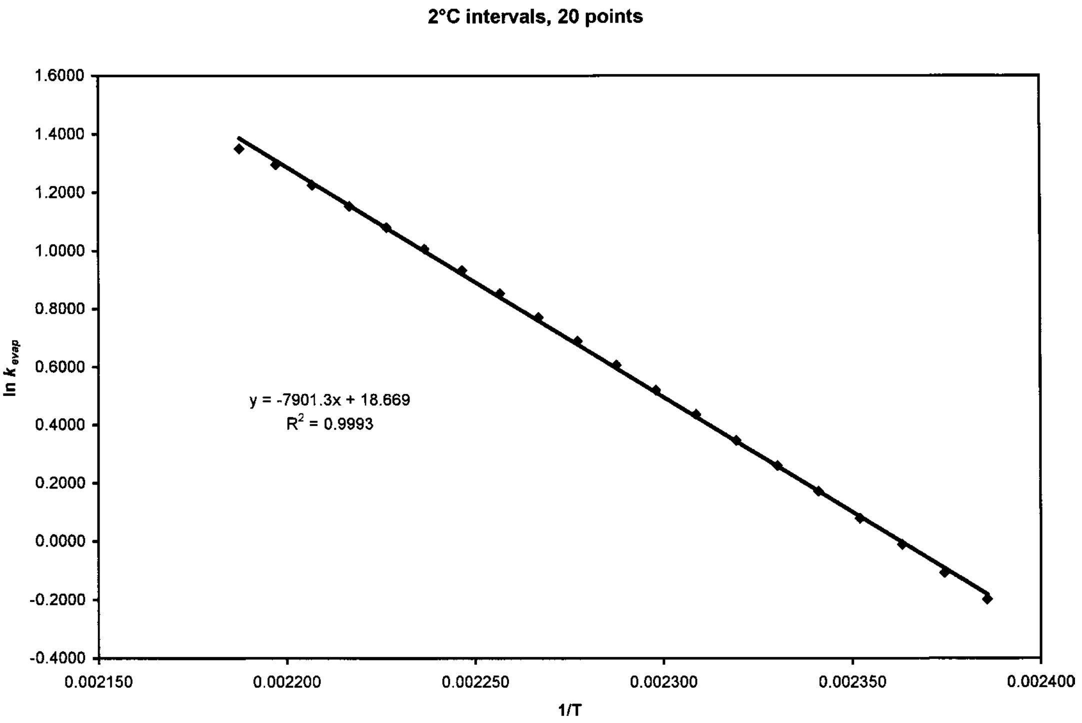

Fig. 9. An Arrhenius plot for benzophenone data taken at 2°C intervals, which includes 20 data points.

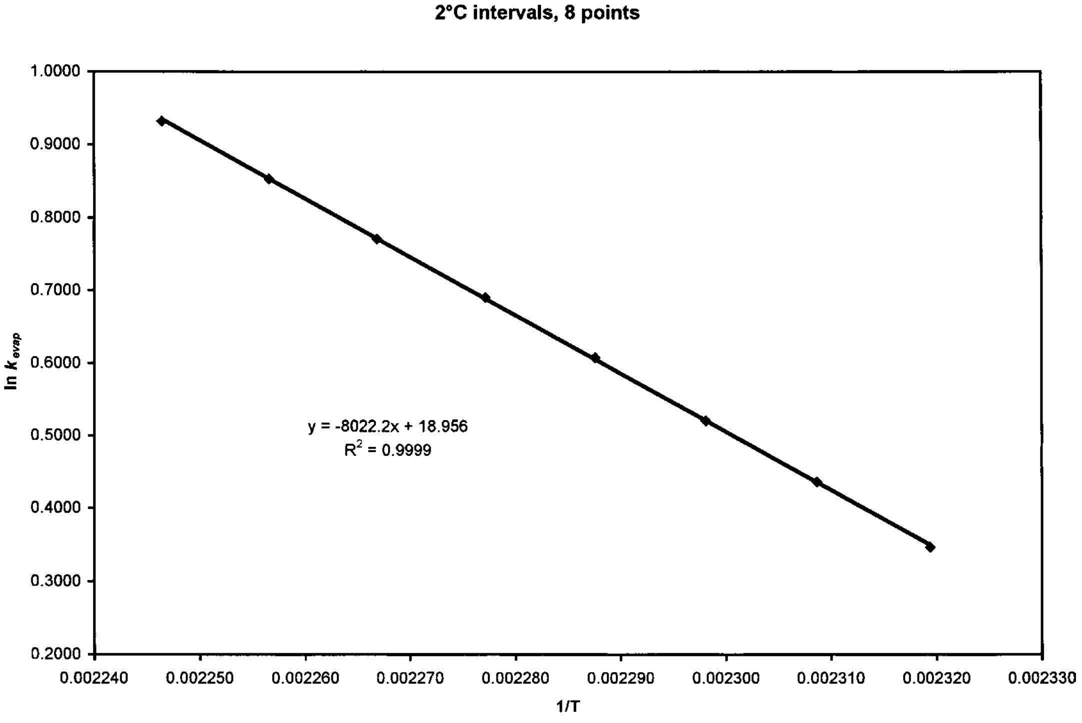

Fig. 10. An Arrhenius plot for benzophenone data taken at 2°C intervals, which includes eight data points.

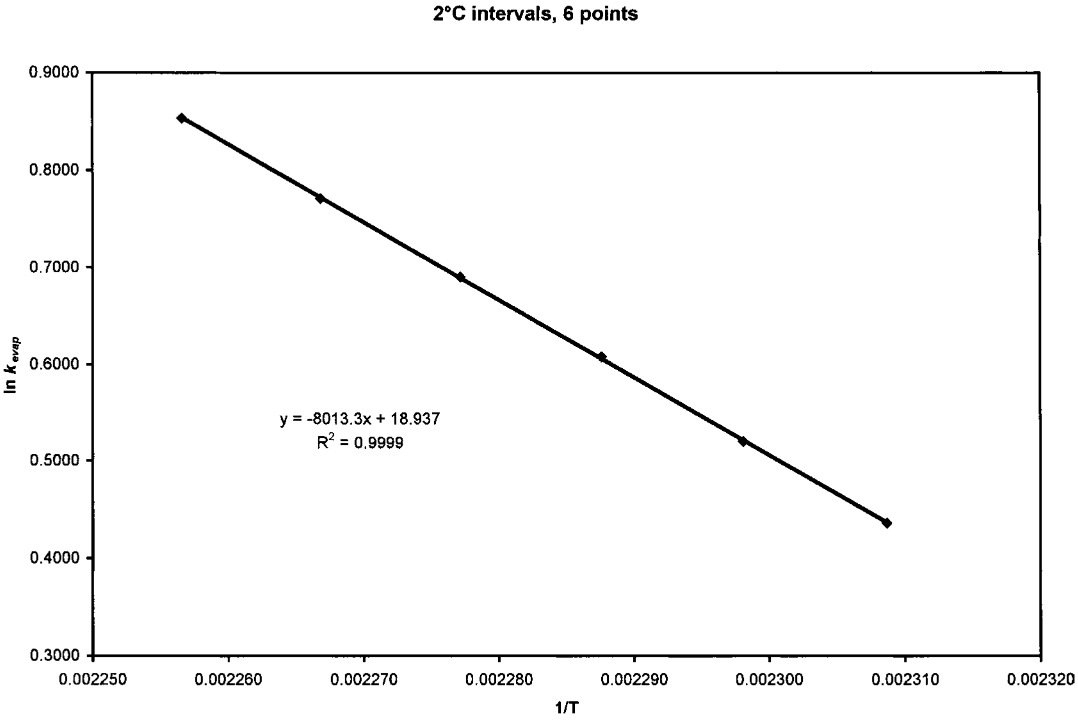

Fig. 11. An Arrhenius plot for benzophenone data taken at 2°C intervals, which includes six data points.

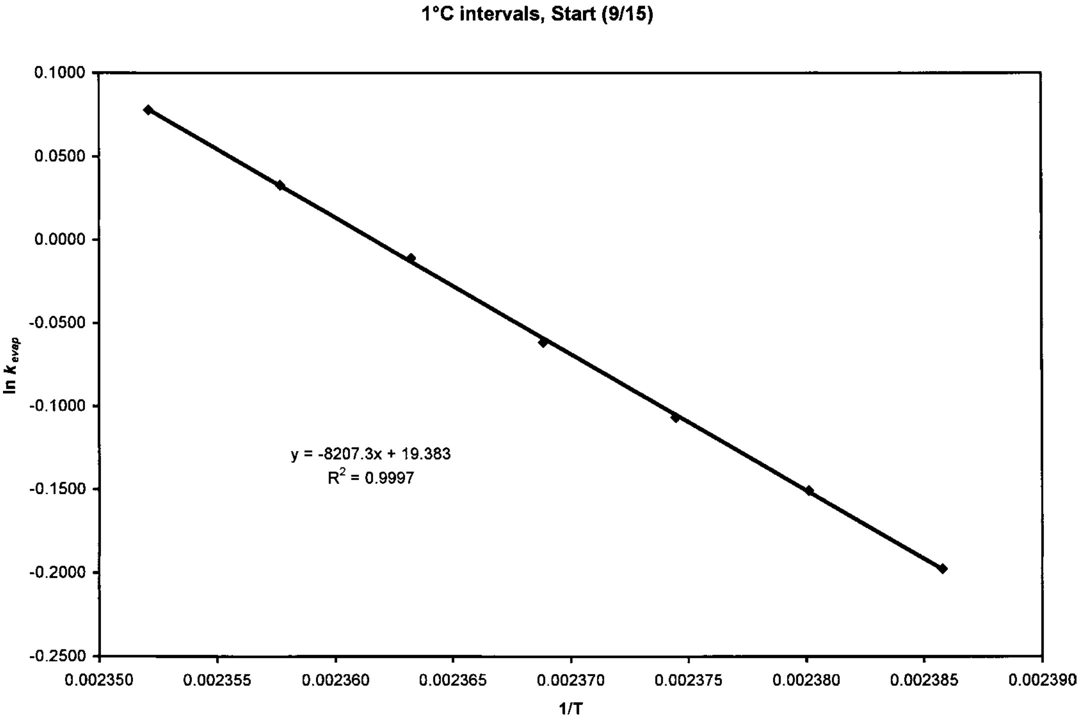

Fig. 12. An Arrhenius plot for benzophenone data taken at 1°C intervals, which includes data points 9–15, designated as the "start" portion.

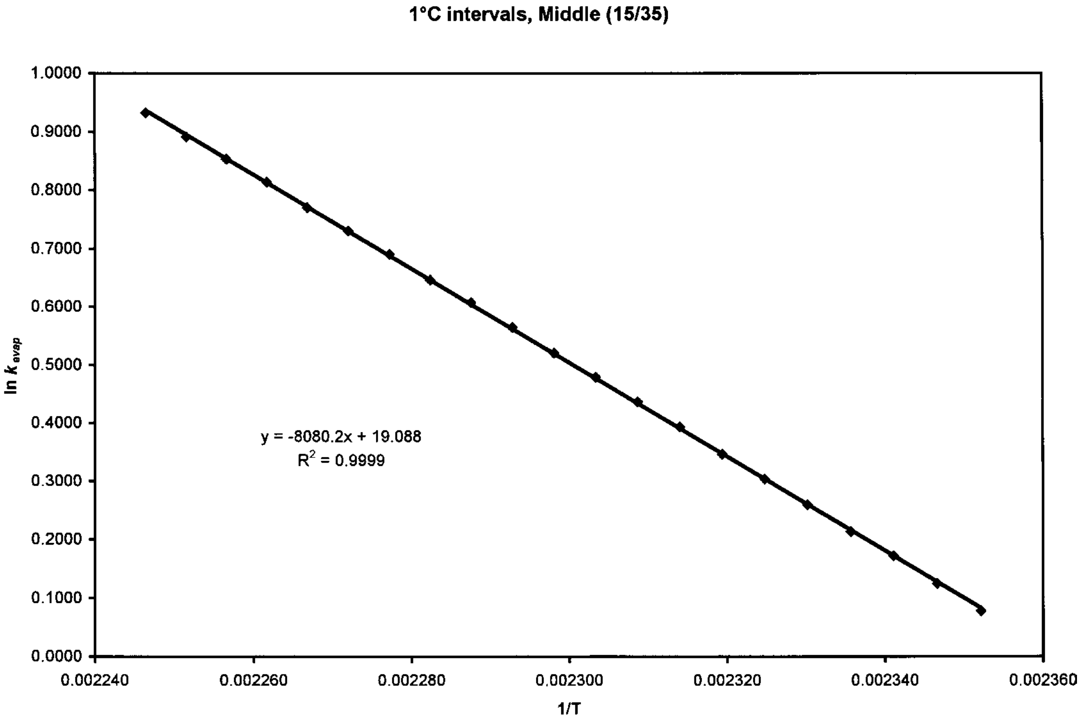

Fig. 13. An Arrhenius plot for benzophenone data taken at 1°C intervals, which includes data points 15–35, designated as the "middle" portion.

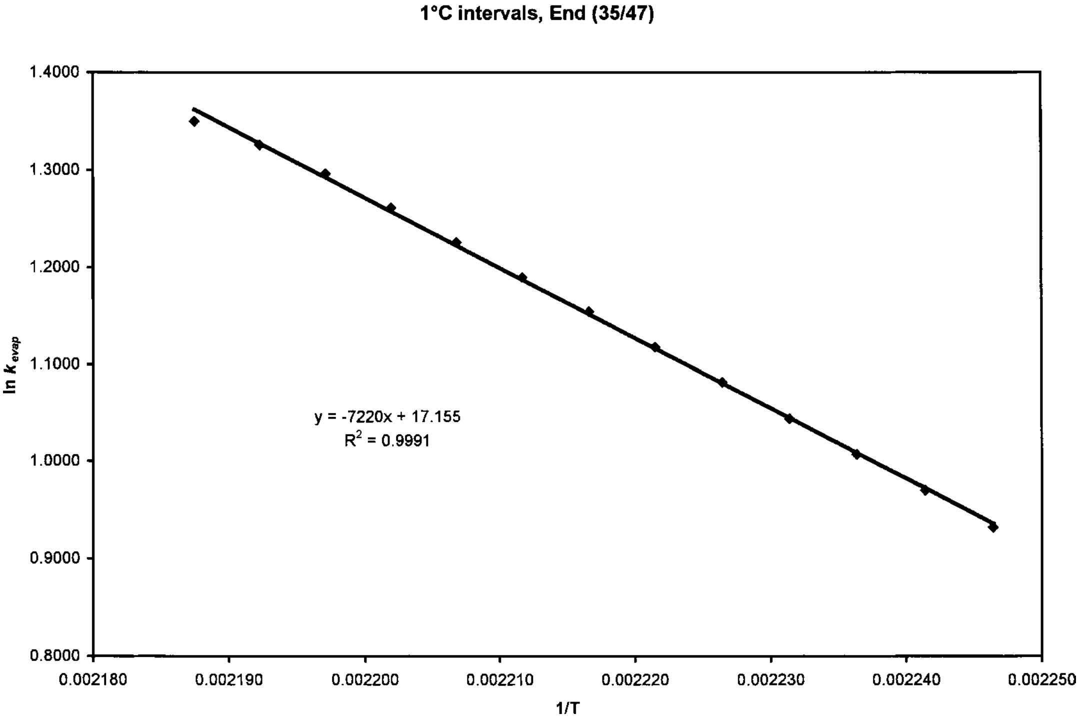

Fig. 14. An Arrhenius plot for benzophenone data taken at 1°C intervals, which includes data points 35–47, designated as the "end" portion.

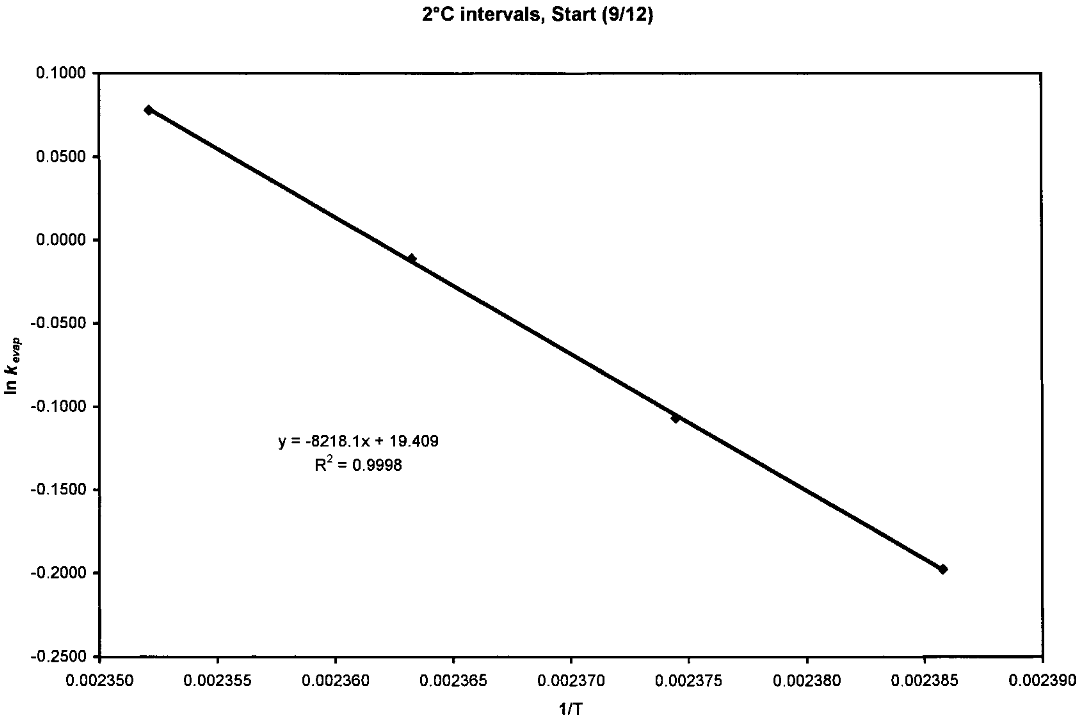

Fig. 15. An Arrhenius plot for benzophenone data taken at 2°C intervals, which includes data points 9–12, designated as the “start” portion.

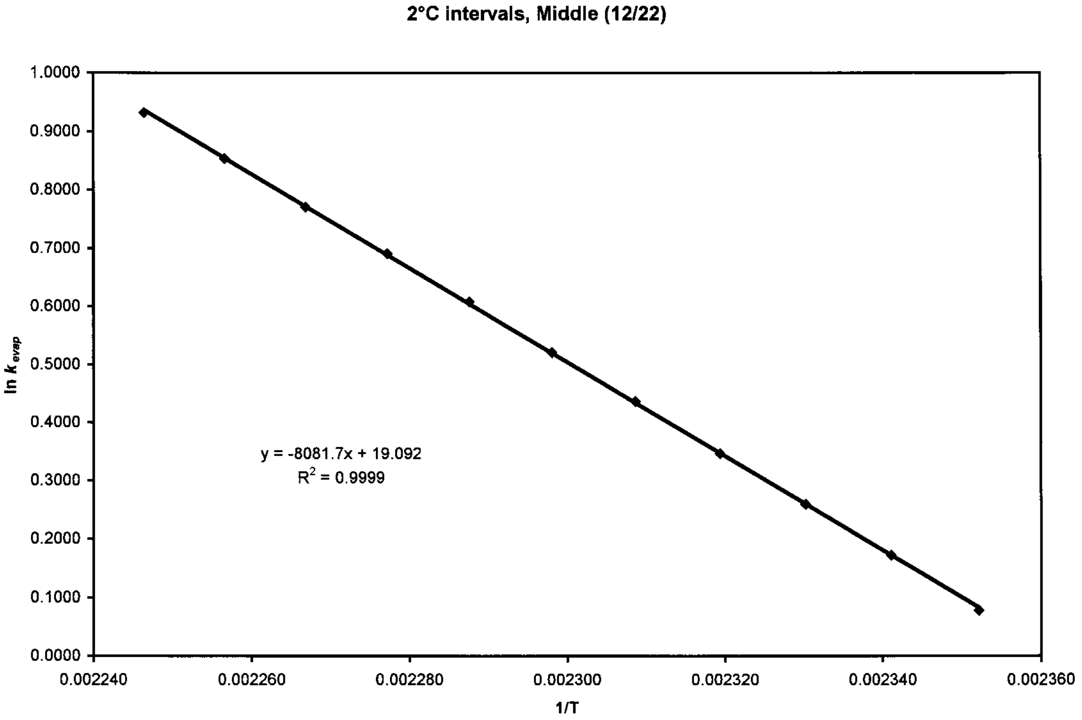

Fig. 16. An Arrhenius plot for benzophenone data taken at 2°C intervals, which includes data points 12–22, designated as the “middle” portion.

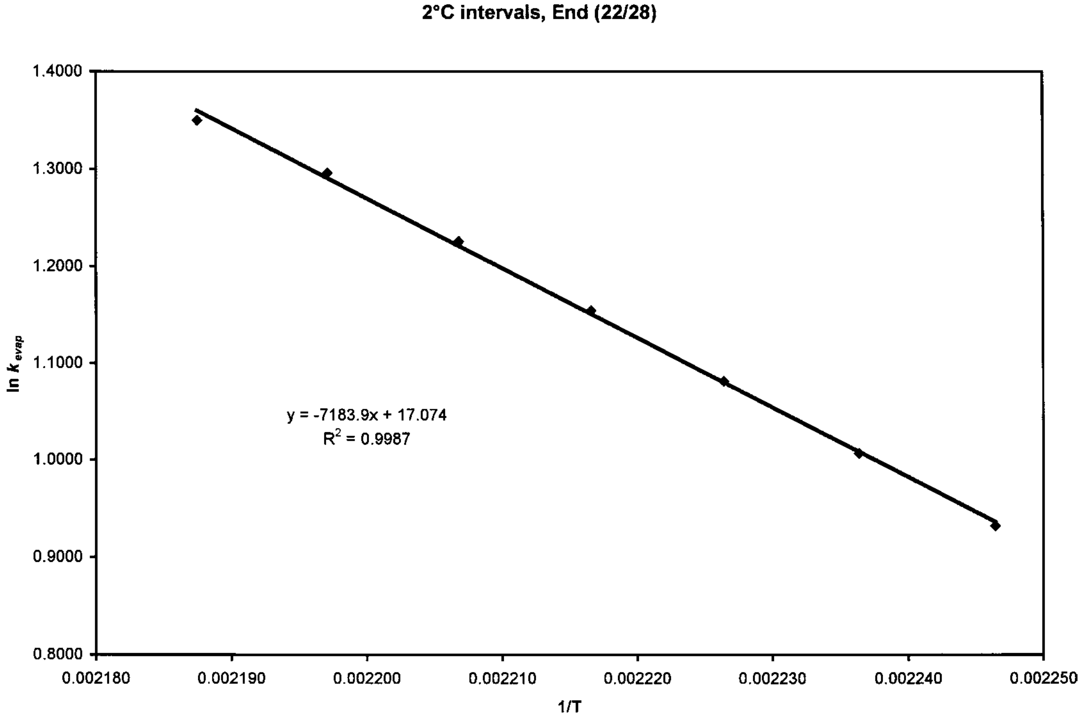

Fig. 17. An Arrhenius plot for benzophenone data taken at 2°C intervals, which includes data points 22–28, designated as the "end" portion.

employed, it is recommended that data points be collected at 0.5°C intervals for several reasons. Taking data points at 0.5°C ensures that the data sample is a good representation of the raw data and it also eliminates the need for trying to determine the optimum number of data points to be used to get a meaningful *R*-square value. A further observation from this study is that the middle region of most kinetic plots correspond to evaporation of a sample of interest from a constant interface. This leads to the conclusion that any corresponding values calculated from this data interval would be precise, if not accurate.

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