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Thermochimica Acta 340–341 (1999) 77–87

thermochimica acta

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The determination of kinetic parameters from DTG curves — fact or fiction?

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Accepted 6 August 1999

Abstract

One way to determine the kinetic parameters of a reaction with an associated loss in mass is by the production of a log plot viz. $\ln[(d\alpha/dt)/(\mathrm{fn}(\alpha))] = \ln A - E/(RT)$. The situation that arises when two or more reactions are occurring simultaneously is discussed. It is shown that the log plot can often help to elucidate that a complex reaction is proceeding, even when this is not obvious from the shape of the DTG curve. The influence on the shape of the log plot, when the activation energy E and/or the pre-exponential constant A varies either with temperature or extent of reaction, is discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Activation energy; Pre-exponential constant; Reaction equations; DTG curves; Computer programs

1. Introduction

A method frequently used to determine the values of A, the pre-exponential constant and E/R the activation energy/gas constant for reactions in which loss of mass occurs, is to determine the intercept and slope respectively of the following equation:

$$\ln[(d\alpha/dt)/(\mathrm{fn}(\alpha))] = \ln A - E/(RT), \tag{1}$$

where values of $d\alpha/dt$, the rate of mass loss, and T, the absolute temperature (K) can be obtained from the DTG curve for the specimen under investigation. The $\mathrm{fn}(\alpha)$ is determined by the particular reaction mechanism which is proceeding. A list of such reaction equations was given originally by Sharp et al. [1] and was later modified by Keattch and Dollimore [2] and Brown [3]. Only 1st order reaction equations will be considered in this paper, so that Eq. (1) can be written as:

$$\ln[(d\alpha/dt)/(1-\alpha)] = \ln A - E/RT. \tag{2}$$

Thus if the reaction under consideration is known to follow a first order reaction mechanism, then a plot of the left-hand side of Eq. (2) versus $1/T$ should give a straight line of slope $-E/R$ and intercept $\ln A$. Sometimes, it has been observed [4] that a plot of this equation produces a line which is relatively linear over most of its length but has a decided curvature or "hump" over a short part of the curve, usually at the high temperature end of the curve. Because most of the curve is linear, it is tempting to ignore the curvature or hump and assume that the slope of the linear portion of the curve gives the true value of the activation energy E.

This paper will indicate how erroneous such a technique can be and that the shape of the log plot can often be used to advantage, to indicate that other reactions may be causing the non-linear shape of the plot.

PII: S0040-6031(99)00255-5

2. Calculations

2.1. Multiple simultaneous reactions

It is often very difficult to detect when more than one reaction is occurring simultaneously from a simple inspection of experimental DTG curves. A computer program [5] has been used to generate two similar 1st order reaction DTG curves which are occurring simultaneously within the same temperature range but which have different peak heights (Fig. 1). The figure shows both the individual curves together with the sum of the two curves and indicates how difficult it is to identify that there are, in fact, two separate reactions taking place from a simple inspection of this curve. Indeed, the summation curve could be fairly easily identified as a single first order reaction. If, however, a plot of $\ln[(d\alpha/dt)/(1-\alpha)]$ versus $1/T$ is plotted, the line produced is far from linear (Fig. 2) showing a "hump" at the high temperature end of the curve. Because the low temperature end of the plot (the right-hand end) appears to be linear it is tempting to use the slope of this portion of the curve to determine E/R. However, this gives an erroneous value for E/R. Log plots for the individual reaction mechanisms produce straight lines (Fig. 3), each having the value of E/R used in the computer program.

Taking the slope of the linear portion of the log plot generated by the data for the combined curve gives a value of E/R which is closer in value to that for the smaller DTG peak, not, as might be expected, a value close to that for the larger of the two peaks. Similar effects occur when more than two 1st order reaction equations overlap but then it is usually more obvious that the total reaction is complex, as the overall shape of the DTG curve is often different to that for a first order reaction equation alone. In Fig. 4, it is noticeable that the overall reaction is not a characteristic first order reaction because it has an unusually wide skirt to the DTG peak.

The log plot (Fig. 5) for the sum of these three first order reaction equations shows a typical "hump", as observed on the example of the sum of the two reactions, except that the "hump" is more pronounced. Note again that the slope of the log plot for the sum of the three reactions is closer in value to the slope of the log plot for the single reaction equation that has the lowest E value.

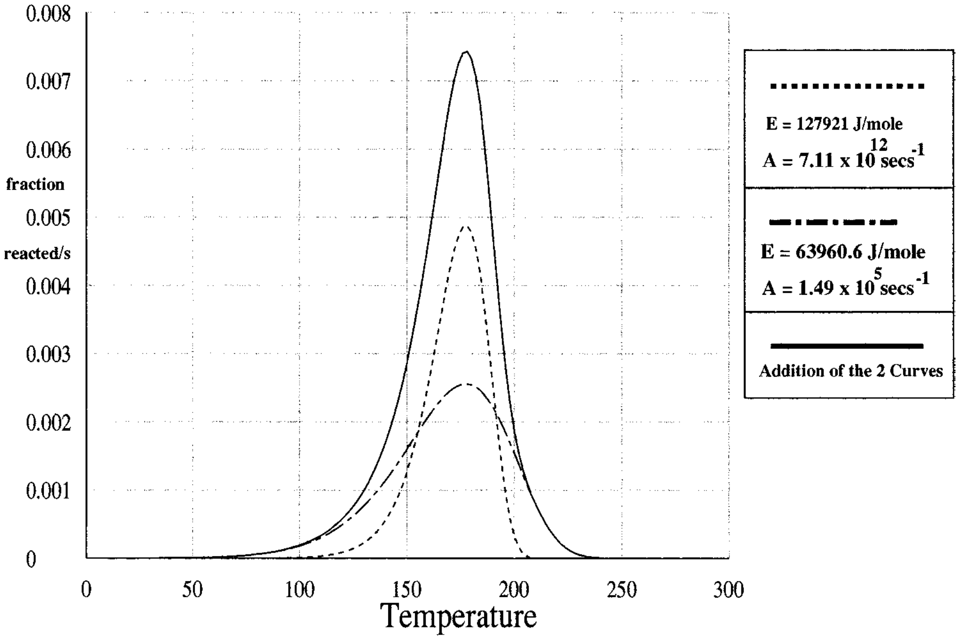

Fig. 1. The resultant curve from the addition of two 1st order curves.

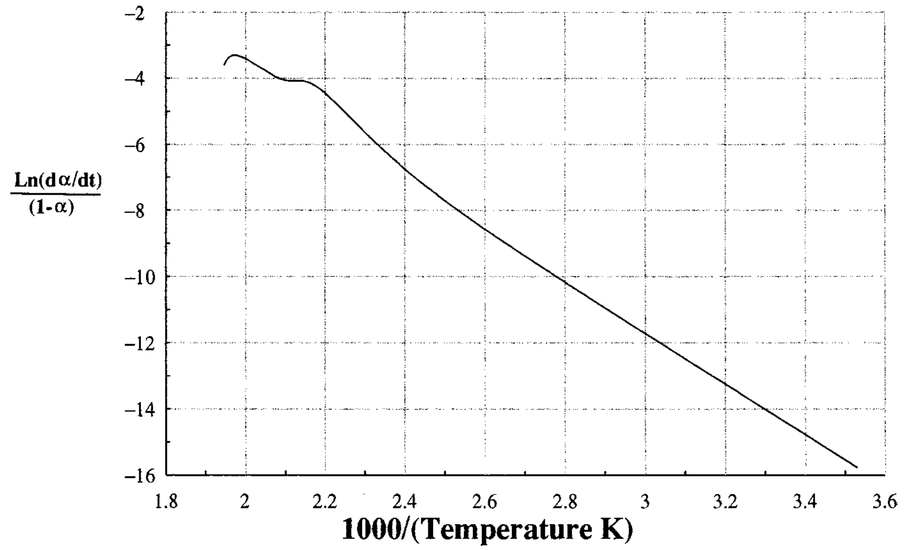

Fig. 2. Log plot for the data for the summation curve of Fig. 1.

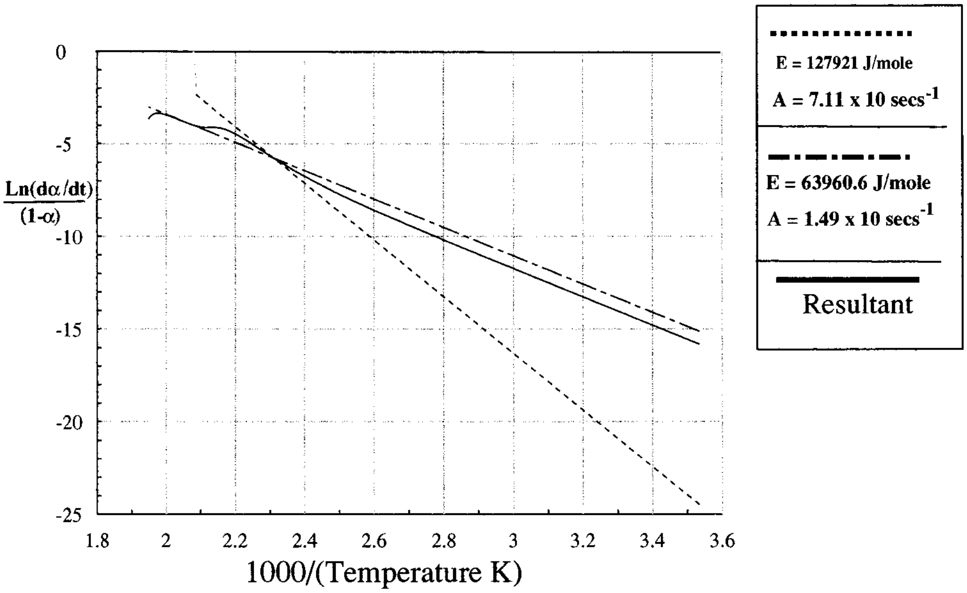

Fig. 3. Individual and total log plots for curves in Fig. 1.

2.2. *Variation of E with temperature*

Various equations relating E with temperature have been examined:

2.2.1. $E = E_0(1 + 0.001(T - T_s))$

Fig. 6 shows a computer generated DTG curve for a first order reaction equation in which the activation energy E increases linearly from 150 to 210 kJ mol^{-1}

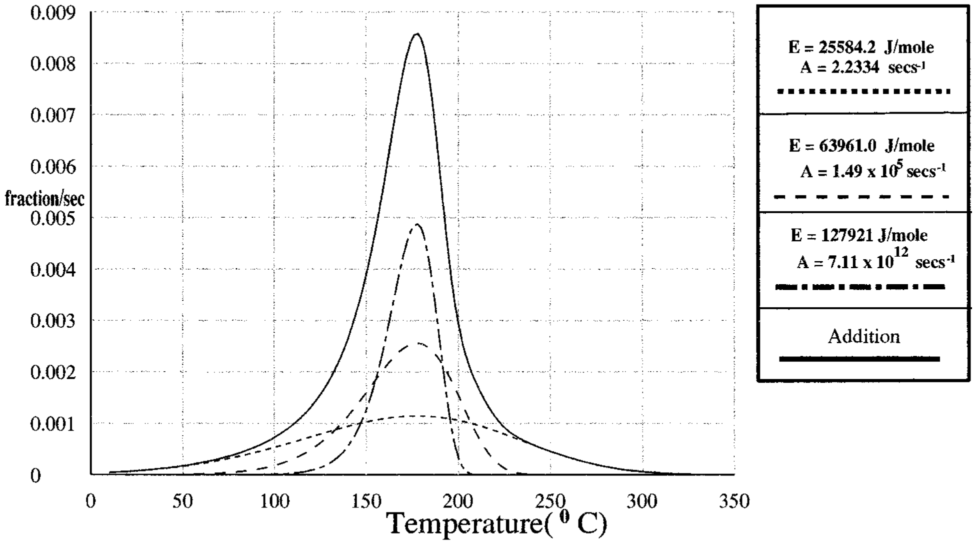

Fig. 4. Addition of three 1st order reactions.

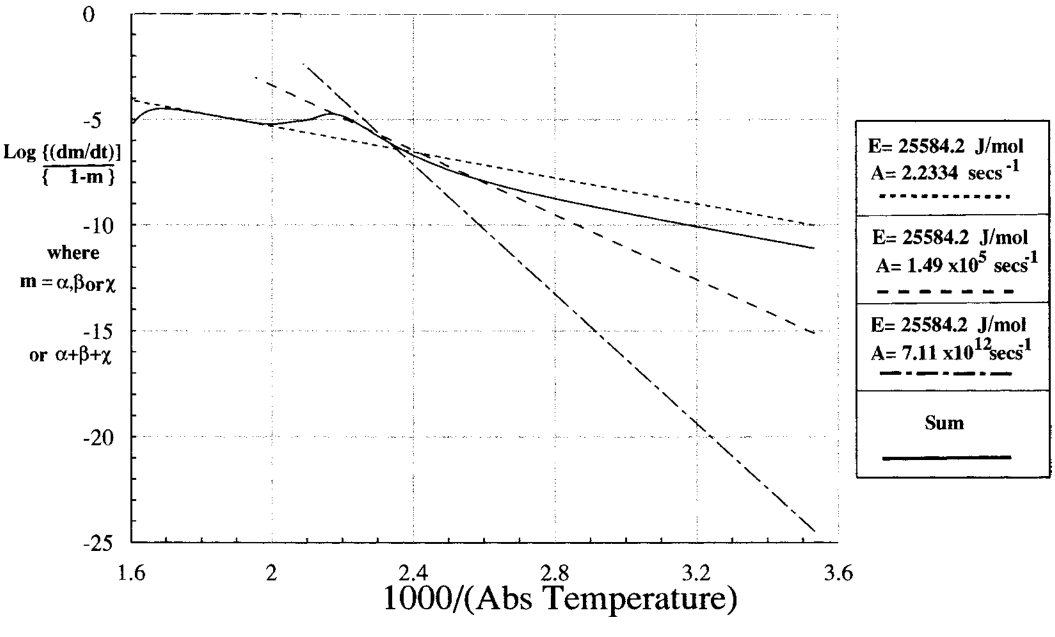

Fig. 5. Log plots for the curves of Fig. 4.

with increasing temperature. This has been directly compared with a similar curve for the case when E is constant at 150 J mol^{-1}. The DTG curve for E increasing, as compared to that when E is constant, is much broader and lower in peak height and has moved to a higher temperature range. Fig. 7 shows the log plots for the data from these DTG curves. Although the lines are *straight*, the slope ($-E/R$) for the log plot when E

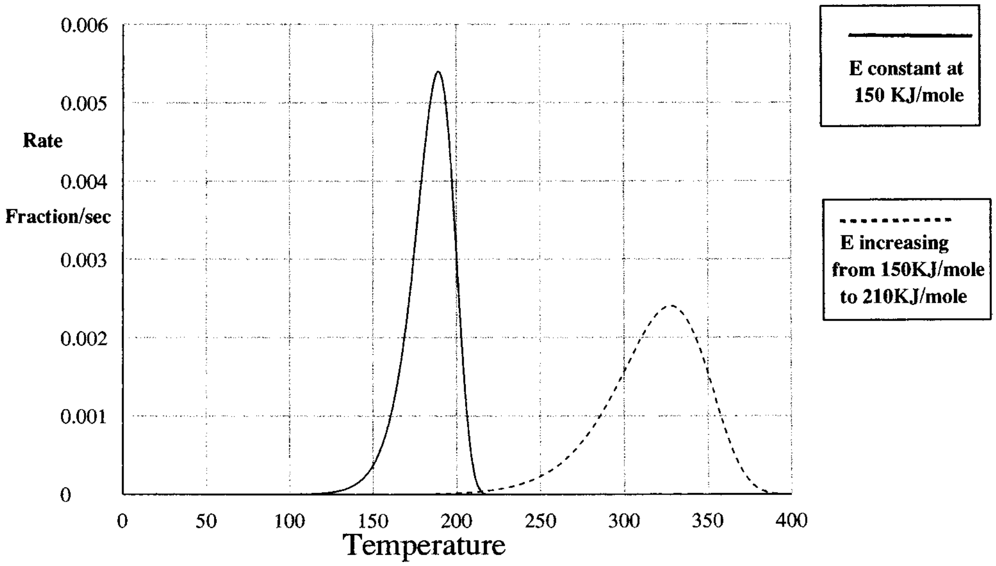

Fig. 6. E increasing linearly with temperature.

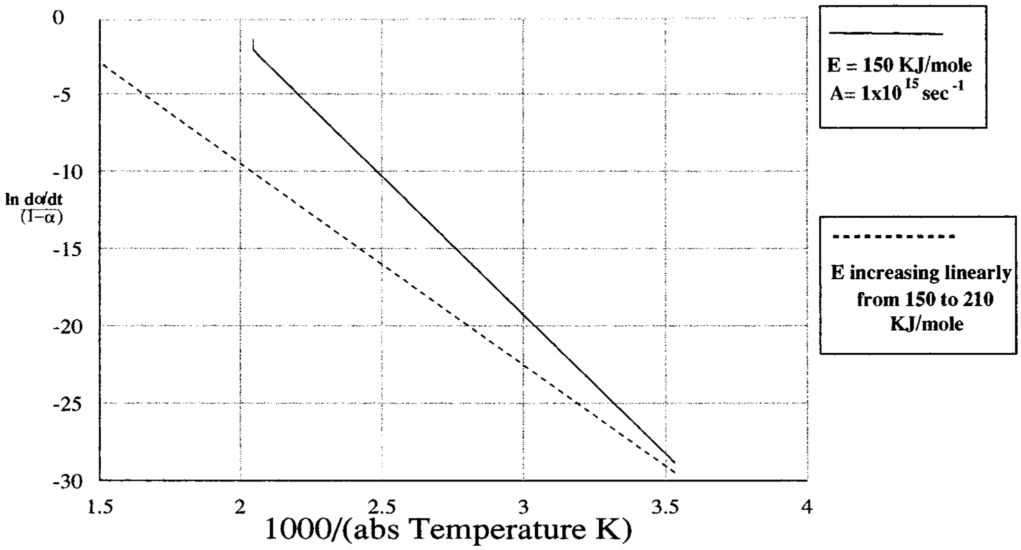

Fig. 7. Log functions for curves of Fig. 6.

varies, gives an erroneous value of E of 107.7 kJ mol^{-1}, much below the variable values of E used in the computer generated DTG curves.

2.2.2. $E=E_0(1-0.001(T-T_s))$

Reverse effects to those observed in Section 2.2.1 are observed when the value of E is decreasing linearly with temperature from 150 to 128 kJ mol^{-1}, the DTG curve moving to lower temperatures (Fig. 8) as compared with the DTG curve for E remaining constant. The curve for variable E is narrower and increased in height.

However, the "best straight line" for the log plot (note that again the plot is linear) shown in Fig. 9.

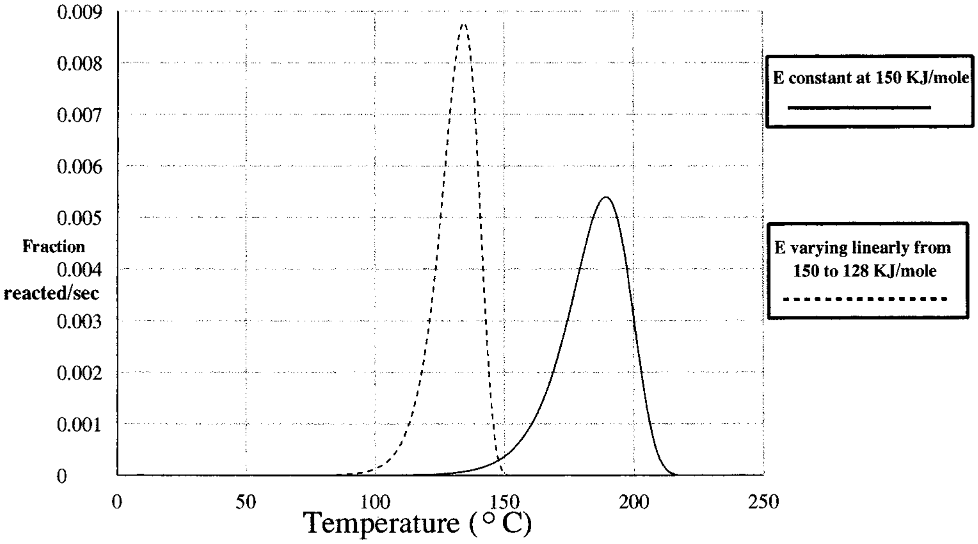

Fig. 8. E decreasing linearly with temperature.

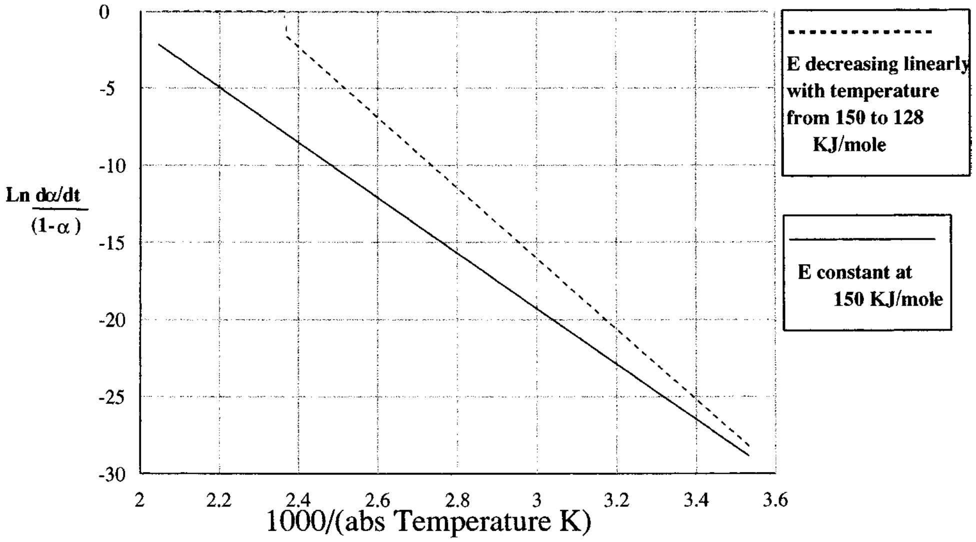

Fig. 9. Log functions for curves of Fig. 8.

gives a value of E of 191 kJ mol^{-1} much higher even than the highest initial value of E used for the generation of the DTG curve. However, there is no indication that the value of E is varying, for the log plot is linear, as it would be for a constant value of E, but giving an incorrect value of E.

2.2.3. $E = E_0(1 + 10^{-6}(T{-}T_s)^2)$

The computer generated DTG curve for a first order reaction in which E increases according to a square law relationship with temperature from 150 to 158.8 kJ mol^{-1} is shown in Fig. 10, together with a similar curve when E is constant at 150 kJ mol^{-1}. The

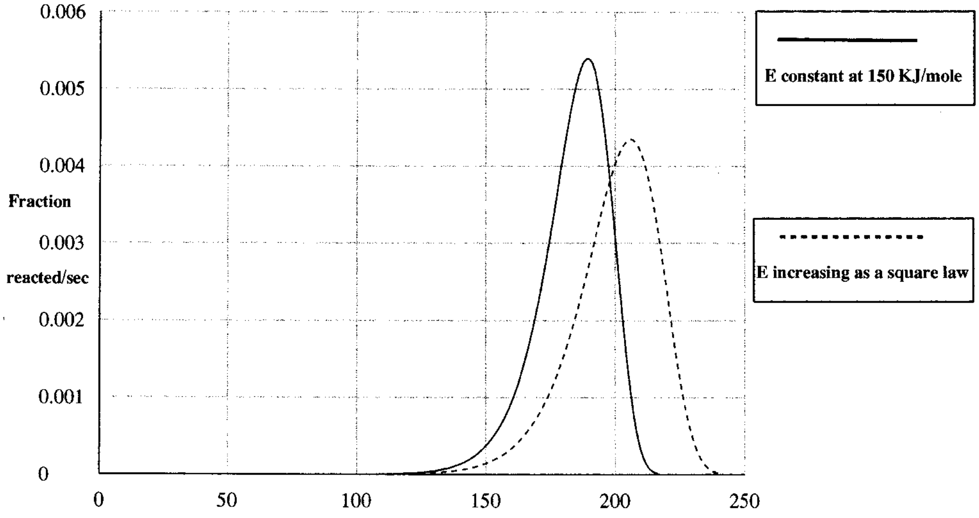

Fig. 10. E increasing with temperature as the square of temperature.

DTG curve for varying E occurs in a higher temperature range and is broader and also reduced in height compared with that for constant E. The log plots for these data (Fig. 11) show that when E is increasing with the square of the temperature, then the log plot is curved towards the abscissa. Using the "best straight line" technique on the curved log plot gives a value of E of 139.2 kJ mol^{-1}, a value which is lower than the initial value of 150 kJ mol^{-1}. The curvature of the log plot could be used to indicate that E is not constant and

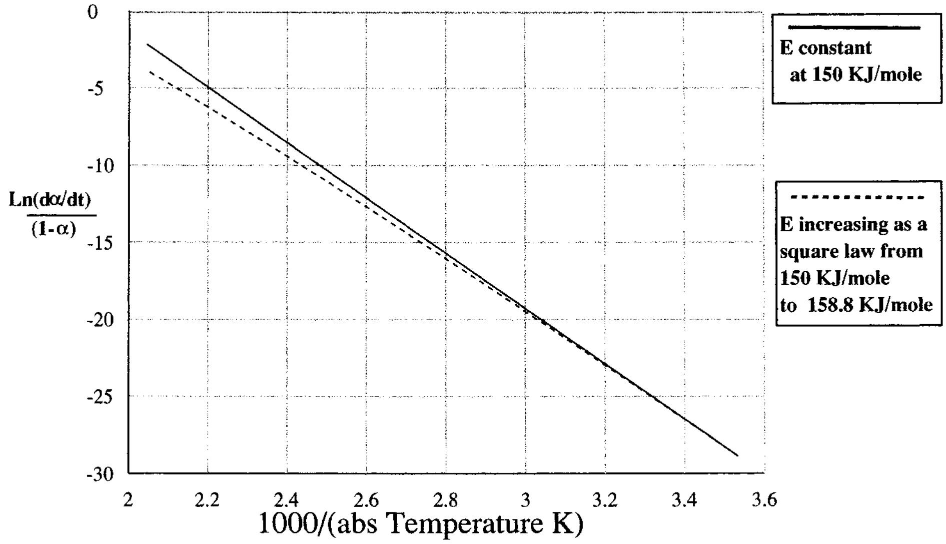

Fig. 11. Log functions for curves of Fig. 10.

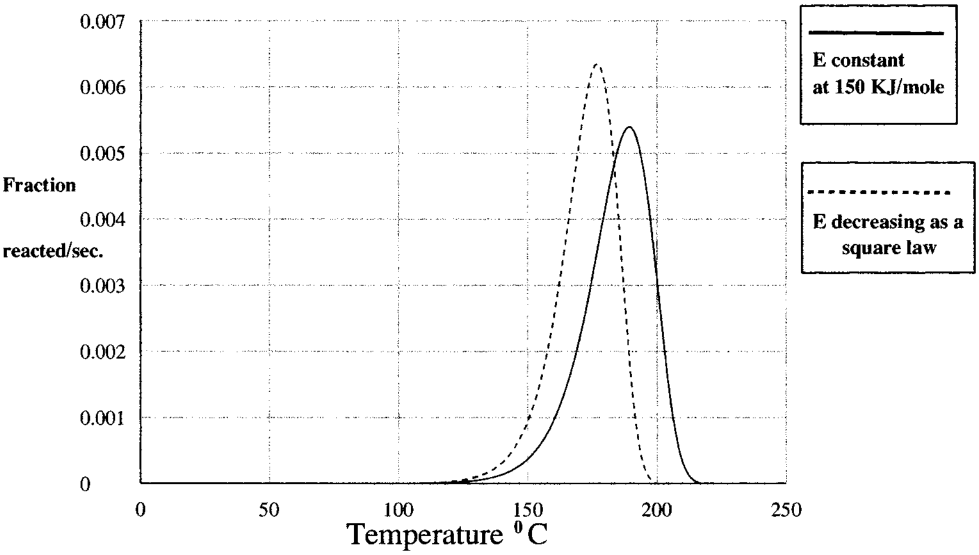

Fig. 12. E decreasing with temperature as the square of temperature.

would suggest that further investigation is necessary before an informed decision about the value of E is made.

2.2.4. $E = E_0(1-10^{-6})(T-T_s)^2$

The computer generated DTG curve for a first order reaction in which E decreases according to a square law relationship with temperature from 150 to 144 kJ mol^{-1} occurs at lower temperatures (Fig. 12) and is sharper and increased in height compared to a DTG curve in which E is constant at 150 kJ mol^{-1} . The log plot (Fig. 13) curves upwards from the abscissa and the slope of the “best straight line” has a value for E of 159 kJ mol^{-1}, which is greater than the initial (and maximum) value of E used for the generation of the data for the DTG curve. As in

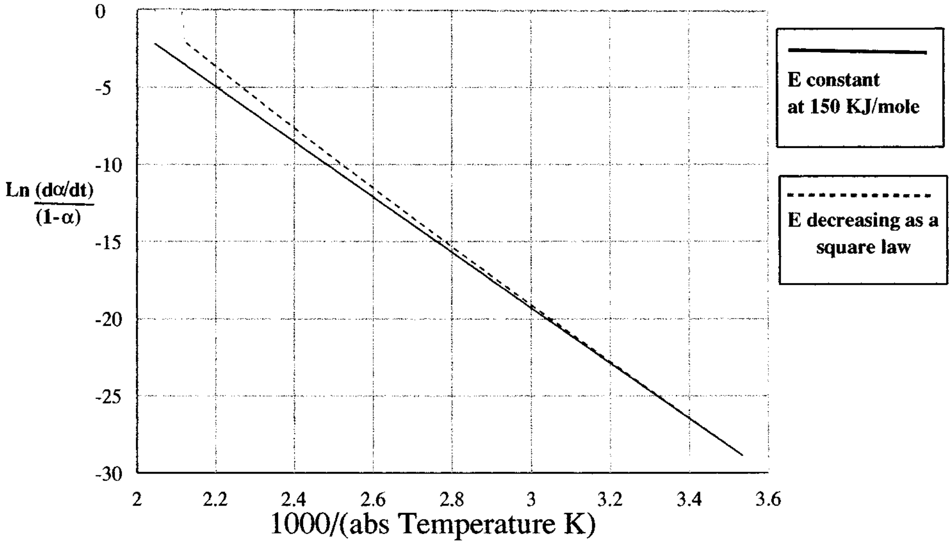

Fig. 13. Log functions for curves of Fig. 12.

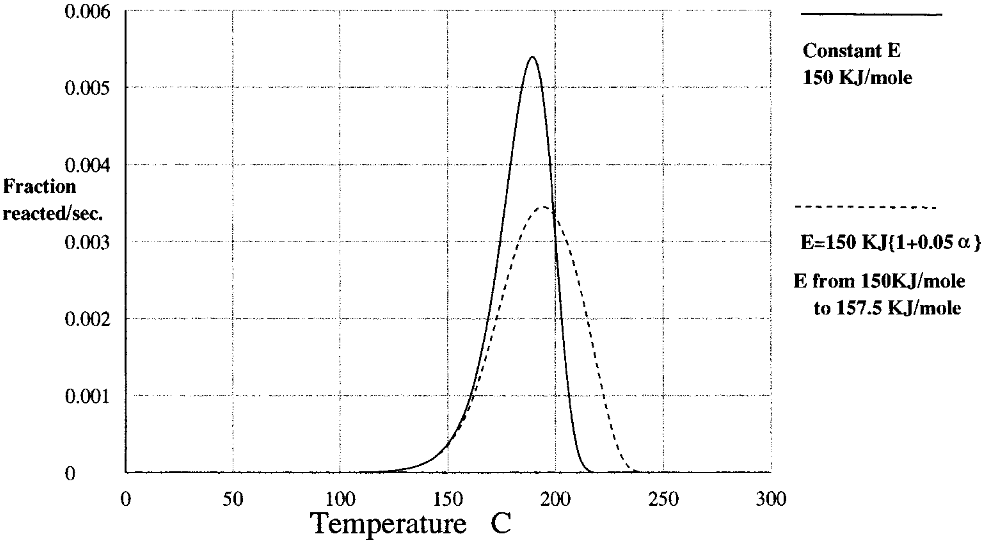

Fig. 14. E increasing linearly with extent of reaction.

Section 2.2.3 above, the curvature of the log plot might again suggest that E is not constant and that further investigation is desirable.

2.3. Variation of E with extent of reaction

Various equations relating E with the extent of reaction have been investigated.

2.3.1. $E = E_0(1 + 0.05\alpha)$

The computer generated DTG curve for a first order reaction in which E increases linearly with the extent of reaction from 150 to 157.5 kJ mol^{-1} is shown in Fig. 14. With varying E as compared with a constant E at 150 kJ mol^{-1}, the DTG curve occurs in a higher temperature range, is broader in size, and reduced in height. The log plot for the

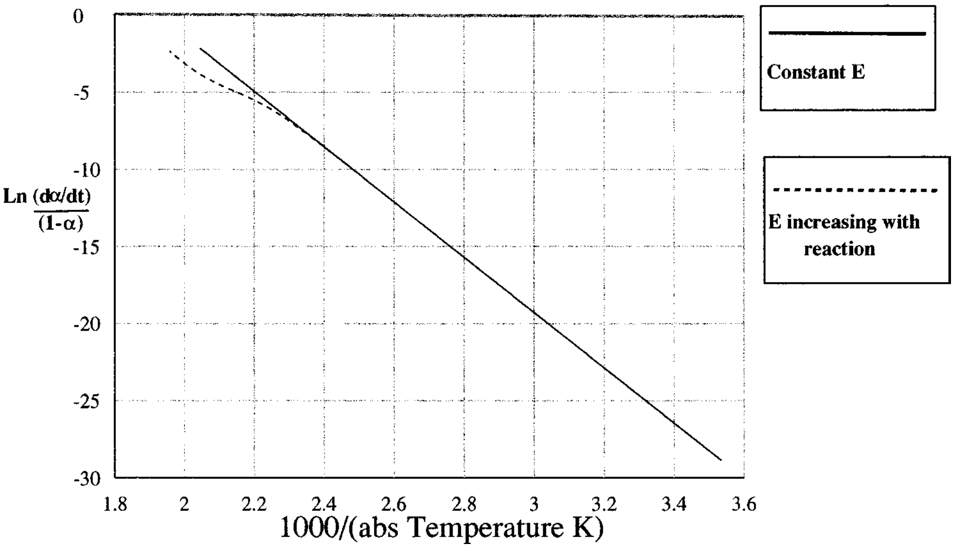

Fig. 15. Log functions for curves of Fig. 14.

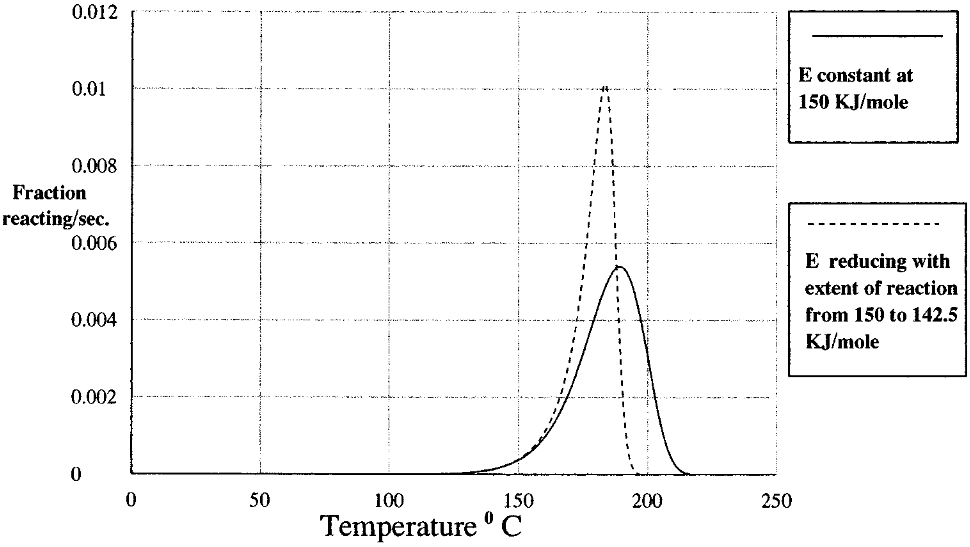

Fig. 16. E decreasing linearly with extent of reaction.

variable E case (Fig. 15) initially follows the log plot for constant E, but then deviates sharply towards the abscissa as the reaction proceeds (left-hand end of graph). If this deviation is ignored when determining the slope of the line, then the value found for E is the initial value E_0. Because this part of the log plot is linear, it might lead to the suggestion that the value of E is constant, were it not for the deviation at the left-hand of the log graph. However, this deviation indicates that the value of E is not constant, although its precise variation would be difficult to identify.

2.3.2. $E = E_0(1-0.05\alpha)$

When E decreases linearly with the extent of the reaction from 150 to 142.5 kJ mol^{-1}, the DTG curve occurs in a lower temperature range, is sharper, and increased in height, compared with that generated for constant E at 150 kJ mol^{-1}, as shown in Fig. 16. The log plots are shown in Fig. 17. The two plots follow each other closely at the low temperature end of the plots, but that for variable E deviates sharply away from the abscissa as the reaction proceeds. The comments made in Section 2.3.1 concerning the value of E apply here also.

3. Conclusions

If a reaction with an associated loss in mass is known to be a first order reaction, a plot of the equation $\ln[(d\alpha/dt)/(1-\alpha)] = \ln A - E/RT$ will only give a linear line of slope $-E/R$, if:

1. there is only one reaction taking place,
2. E is constant over the whole temperature range of the reaction, and
3. E does not vary with the extent of reaction.

The shape of a non-linear log plot can sometimes indicate that the decomposition process is not a simple one. A "hump" in an otherwise linear plot may indicate that there is more than one reaction occurring simultaneously. This "hump" is more pronounced as the number of reactions occurring simultaneously increases. If, when determining the "best straight line", the presence of the "hump" is ignored, then the value of the slope of the log curve approaches that of the reaction with the lowest E value, not as might be expected, that with the maximum value.

If E varies linearly with temperature, then the log plot is also linear but the value of the slope ($-E/R$) bears no relationship to the values of ($-E/R$) calculated from the log plots. For increasing E values, the

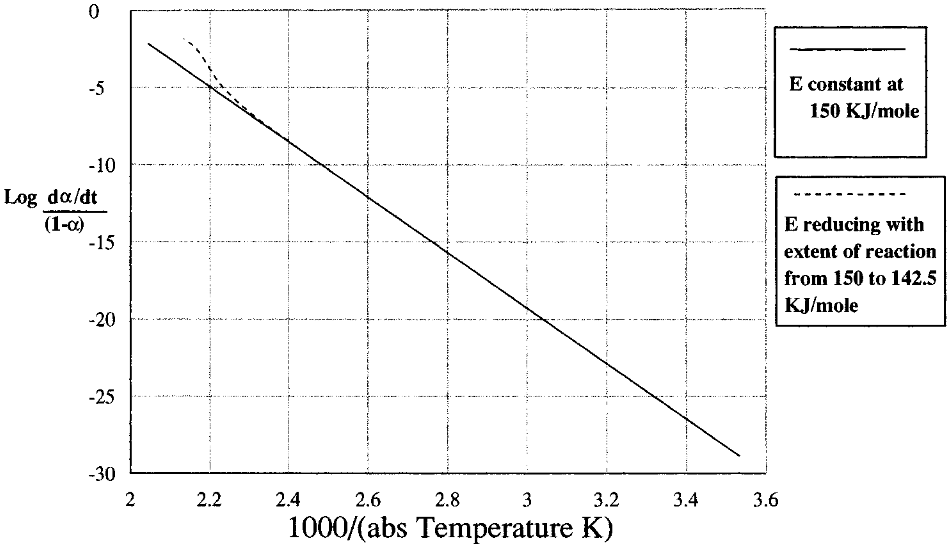

Fig. 17. Log functions for curves of Fig. 16.

slope of the log curve is too low, whereas for decreasing E values, the slope is too high.

Perhaps, as expected, when the value of E varies as the square of temperature then the log plot is non-linear, giving some indication that E is also non-linear.

When the value of E varies with the extent of reaction, the slope of the log plot is virtually the same as that for a fixed value of E, until the fraction reacted approaches 1, when there is a sharp deviation from linearity in the log plot.

Thus it appears that, except for the situation when the value of E varies linearly with temperature, the shape of the log plot can give some indication of simultaneous multiple reactions occurring or variable values of E occurring during a reaction.

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