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Kinetics of overlapping reactions

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Abstract

The effect on the log plot, used to determine the activation energy (E) and the frequency factor (A), when using data derived from DTG peaks from two independent reactions, but which are in close temperature proximity, is discussed. It is shown that, while it is possible to derive activation energy information from such data when the peaks are of nearly equal size, the log plot produced from similar peaks having widely differing peak areas (i.e. widely differing E and A values) is non-linear. In this situation, it is impossible to derive either of the E values. The practice of drawing the statistically best straight line on such log plots has no meaning, and is not to be recommended, because it gives misleading results. Preliminary results from data derived from interacting reactions are also discussed.

Keywords: DTG; Kinetics; Log plots; Reaction equations; Computer program

1. Introduction

Homogeneous reactions at constant temperature proceed according to an equation of the form:

$$g(\alpha) = k_T t \tag{1}$$

where α is the fraction reacted after a time t, k_T being the specific reaction constant at a given temperature T (K) and $f(\alpha)$ a function of the fractional mass at time t. The specific reaction constant is temperature dependent and is given by the following relationship:

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

where A is the frequency factor (s^{-1}), E the activation energy (J/mol) for the process, R the gas constant (J/[mol K]), and T the absolute temperature (K).Combining Eqs (1) and (2)

$$g(\alpha) = A \exp\left(\frac{-E}{RT}\right) t \tag{3}$$

This equation is difficult to manipulate when the temperature is rising, for example in TG, even if the function $g(\alpha)$ is known, for now, α, T and t are all varying. When studying reactions which involve loss in mass, it is usual to plot α against t or T to obtain the TG curve or $\mathrm{d}\alpha/\mathrm{d}t$ against T to obtain the DTG curve.

If Eq. (1) is differentiated:

$$g'(\alpha)\mathrm{d}\alpha = k_T \mathrm{d}t \tag{4}$$

where $g'(\alpha)$ is the first differential of $g'(\alpha)$.

Re-arranging:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{k_T}{g'(\alpha)} \tag{5}$$

The function $1/g'(\alpha)$ is usually written as $f(\alpha)$, so that Eq. (5) can be usually written as:

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$$\frac{d\alpha}{dt} = k_T f(\alpha) \tag{6}$$

If k_T is replaced by the expression of Eq. (2) in Eq. (6), then

$$\frac{d\alpha}{dt} = f(\alpha) A \exp\left(-\frac{E}{RT}\right) \tag{7}$$

This equation is strictly valid only for constant temperatures, whereas the temperature in TG usually varies with time. In most equipment, the change of temperature with time is constant, i.e.

$$\frac{dT}{dt} = \text{constant, usually signified by } \beta \tag{7a}$$

Now,

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} \equiv \beta \frac{d\alpha}{dT}$$

Thus, Eq. (7) can be written as:

$$\frac{d\alpha}{dT} = \frac{f(\alpha)}{\beta} A \exp\left(-\frac{E}{RT}\right) \tag{7b}$$

Taking logarithms

$$\ln\left(\frac{d\alpha/dT}{f(\alpha)}\right) = \ln\left|\frac{A}{\beta}\right| \equiv -\frac{E}{RT} \tag{8}$$

Eq. (7b) is the basic equation used to produce TG and DTG curves [1]. Often, however, $d\alpha/dt$ is often plotted against temperature in commercial equipment, and it is in this form that the equation is used in this paper.

If the correct function $g(\alpha)$ and, hence, $f(\alpha)$ has been chosen for the particular reaction under study, then a plot of ln $[(d\alpha/dt)/f(\alpha)]$ against $1/T$ should produce a straight line of slope $-E/R$ and intercept $\ln A/\beta$. If, however, $d\alpha/dt$ is plotted against temperature, then a plot of ln $[(d\alpha/dt)/f(\alpha)]$ against $1/T$ should produce a straight line of slope $-E/R$ and intercept $\ln A$.

There are various ways of identifying the correct function of α, $g(\alpha)$ to use, but all have their various difficulties.

1. The method of Sharp et al. [2], whereby an isothermal TG experiment is carried out and a plot of α against $t/t_{0.5}$ is made, and compared with standard plots, can be used. However, the method can be time-consuming and for some reactions the shape of the curve is also dependent on the time constants associated with the furnace heating [3].
2. Another method used is to carry out a standard DTG experiment followed by plotting Eq. (8) for each of the functions $g(\alpha)$ and determining $-E/R$ and $\ln A/b$ for the curve which produces the value of the regression coefficient nearest to one when the 'best straight lines' are drawn on every curve.
3. The method of Malek [4], expanding on an earlier suggestion of Kissinger [5,6], suggests the use of a 'shape index' on DTG curves as a means of identifying the kinetic process. Dollimore et al. [7] have reviewed methods of kinetic analysis based on shape factors, emphasizing the significance of onset, peak and final temperatures.

2. Practical considerations

As stated above, all the methods have their limitations, the problems associated with method (2) being blamed on experimental conditions. Although there is often considerable 'noise', particularly on a $d\alpha/dt$ trace, it is usually quite easy to apply a smoothing routine to such data [8–10]. Also, in many instances the 'best straight line' is wrongly used in these calculations. In formal statistics, the 'best straight line' represents a line through a series of points which are scattered uniformly about that line. Many of the ln plots derived from DTG curve data consist of a series of consecutive points on one side of the line, followed by another series on the other side of the line. In this situation, the regression coefficient has no meaning!!

The remainder of this paper will study the reasons why ln plots are often non-linear and will show that these are often due, not to an incorrect choice of $g(\alpha)$, but for other perfectly legitimate reasons which will now be outlined.

3. Linear log plots

The comments made below apply equally well to all reaction equations, but in order to reduce the amount of work required in the production of this paper, only the first-order (F1) and volume-diffusion (D3) reaction equations will be considered.

Evans et al. [11] produced finite difference equations which, when using the standard reaction func-

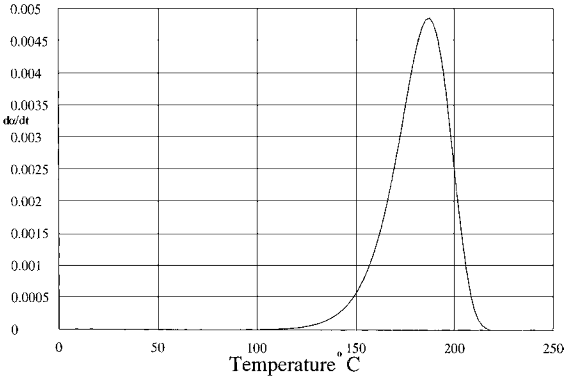

Fig. 1. DTG curve for a single first-order reaction (E=169 kJ/mol, A=1.5×10^{13} s^{-1}).

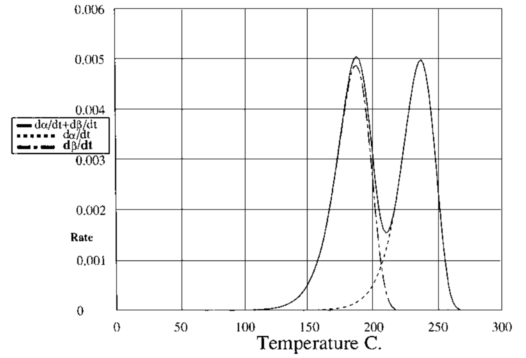

Fig. 3. DTG curves for the two first-order reactions about 50°C apart (E_1=133.6 kJ/mol, E_2=169 kJ/mol A_1=1.5×10^{13} and A_2=1.97×10^{15}).

tions, could reproduce theoretical TG, DTG curves, together with their associated log plots for all the then known functions. If any of the known reaction equations were used to generate the DTG curve and a log plot was obtained from this data, then this curve was always be linear when plotted as [ln (dα/dt)/(α)] against 1/T, having a slope $-E/R$ and intercept ln A equal to that used in the calculations (Figs. 1 and 2).

4. Non-linear log plots

As stated above, many experimental TG and DTG plots do not compare with the calculated TG and DTG plots for any of the given reaction mechanisms, making for difficulties in determining E and ln A from the log plots, for these ln plots are themselves often non-linear. These non linear plots can easily be observed if two DTG peaks are generated theoretically, of equal height and are about 50°C apart. Such a DTG curve is shown in Fig. 3. Fig. 4 shows three log plots, two from the individual peaks (dotted lines) and a third (full line) which is the resultant of the other two curves.

Note that this combined curve is mainly linear along one of the individual log plots, but then switches over fairly rapidly to the other log plot at a higher temperature. In a practical experiment, it is the resultant curve which will be generated. Nevertheless, it would be fairly straightforward to determine the slope and intercept for the two reactions from such a log plot.

Next, we consider what happens to the shape of the log plot if the two peaks of Fig. 3 occur closer together in temperature. If the peaks are of similar height, then the combined log plot is again similar to that of Fig. 4.

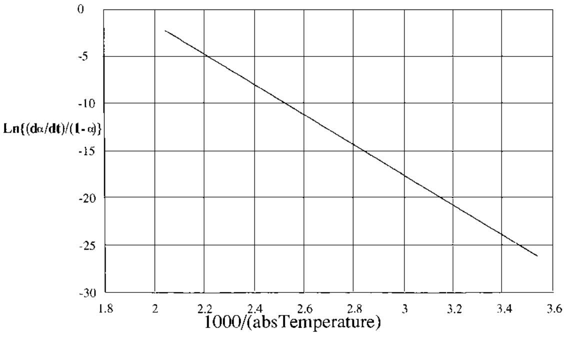

Fig. 2. Log plot for the DTG curve of Fig. 1. Value of E from slope=169 kJ/mol.

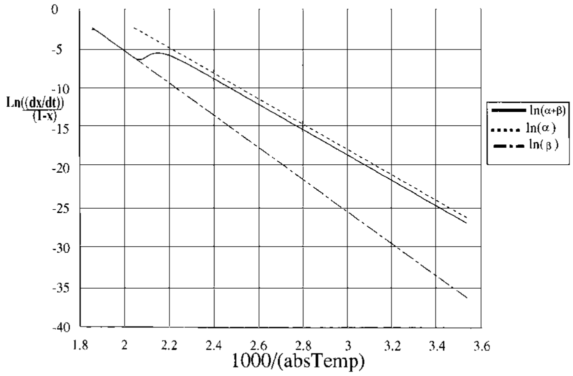

Fig. 4. Log plot for the DTG curves of Fig. 3.

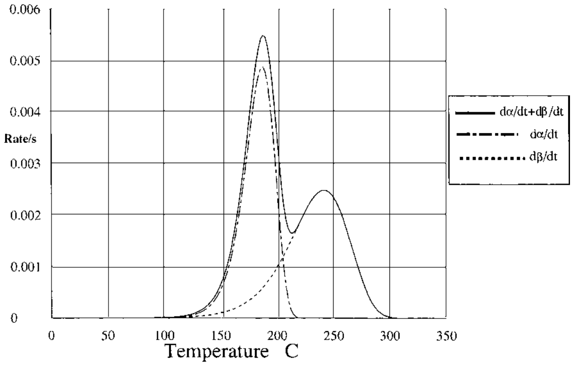

Fig. 5. DTG curves for two overlapping first-order reactions. (E_1= 133.6 kJ/mol, E_2=82 kJ/mol, $A_1=1.5\times10^{13}$ and $A_2=1.17\times10^6$).

with the slopes of the individual lines due to each reaction being almost parallel, because peaks which have the same height and occur at nearly the same temperature will have similar E values. Again, in this situation, it will be relatively easy to distinguish the two linear log plots and so determine the E values for each reaction.

Neighbouring peaks, however, are not always of the same height. Fig. 5 shows two first-order peaks which are unequal in height (due to large differences in the values of activation energy or frequency factor), a situation which is fairly common in practical experiments. In this case, although the individual log plots for the two peaks are linear (Fig. 6), the combined log plot is noticeably curved and there is no way to determine satisfactory values of E or $\ln A$ from such curves. Notice that the curvature of the log plot can change radically with a slight change in the ratio of peak heights (Figs. 7 and 8). This situation appears to be at its worst for neighbouring peaks of different heights, but does show a similar effect for completely overlapping peaks (Fig. 9). In this latter case, it is not immediately obvious that there are two peaks in the same temperature range except for the non-linearity of the log plot (Fig. 10).

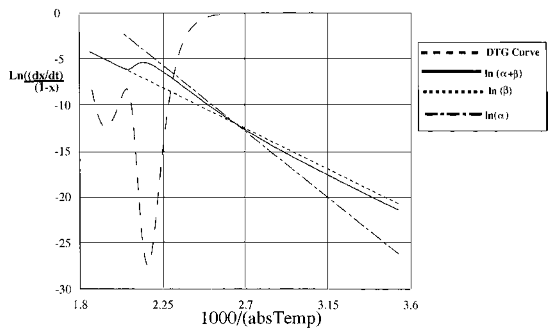

Fig. 6. Log plot for the DTG curves of Fig. 5.

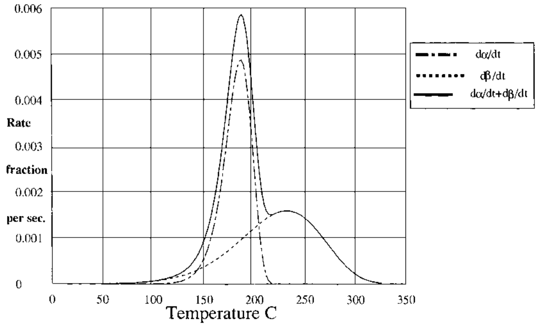

Fig. 7. DTG curves for two overlapping first-order reactions. (E_1= 133.6 kJ/mol, E_2=48 kJ/mol, $A_1=1.5\times10^{13}$ and $A_2=3.46\times10^2$).

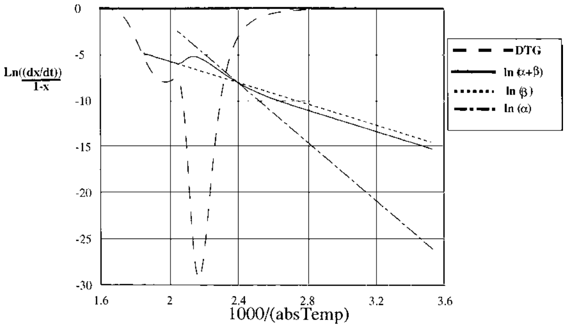

Fig. 8. Log plot for the DTG curves of Fig. 7.

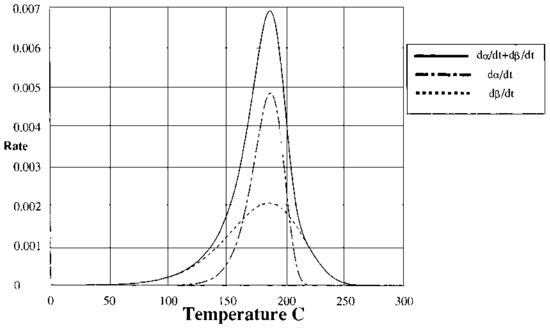

Fig. 9. DTG curves for the two first-order reactions within each other (E_1=133.6 kJ/mol, E_2=53 kJ/mol, $A_1=1.5\times10^{13}$ and $A_2=5\times10^3$).

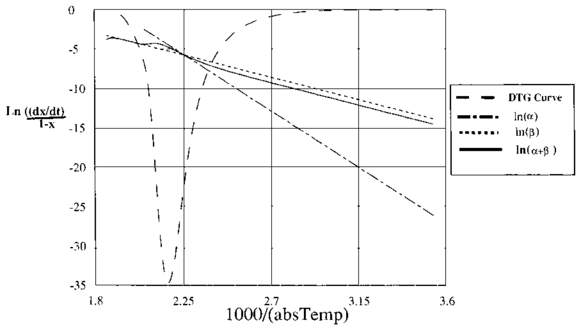

Fig. 10. Log plot for the DTG curves of Fig. 9.

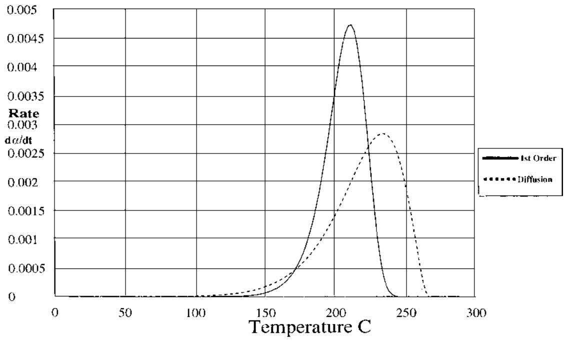

Fig. 11. DTG curve for two independent reactions.

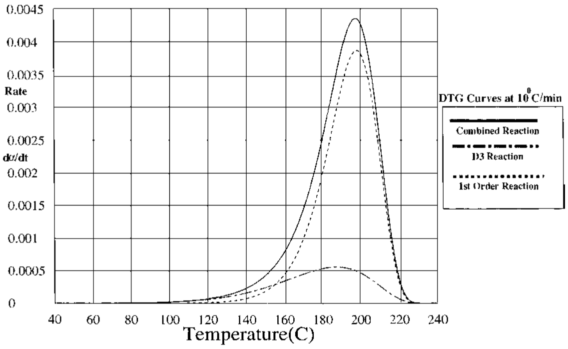

Fig. 12. The effect of competing reactions.

It should be appreciated that when using data derived from theoretical models of the reaction equations, values of dα/dt and α are produced which are far smaller than can usually be obtained in practical experiments. Thus, these log plots extend to much lower temperatures than would be usual in practical work. In order that the theoretical log curves may be compared with practical ones, some of the figures showing log plots (other than that for the single reaction) also contain a scaled version of the DTG curve in order that the temperature position of log plots relative to the DTG curve may be assessed. Thus, the curvature of the log plots of Figs. 6, 8 and 10 would be easily visible on a practical log plot.

5. Competing reactions

Flynn [12] discussed the possible reaction equations which would apply to competing reactions. If the reactions are competing, then they must occur within the same temperature range, for if not, then within a given temperature range only one of the reactions would proceed prior to that reaction at the higher temperature. The equation which was suggested by Flynn [11],

$$\frac{d\alpha}{dt} = (1-\alpha)\left[A_1\exp\left(-\frac{E_1}{RT}\right) + A_2\exp\left(-\frac{E_2}{RT}\right)\right]$$

where A_1 and A_2 are the frequency factors (s^{-1}), and E_1 and E_2 are the activation energies associated with each reaction, has been used in the finite difference equations [10] to produce the resultant DTG curve.

The two reactions — one, a first-order reaction (F1), and the other a volume-diffusion reaction (D3) — which, if they were non-competitive would have DTG peak temperatures fairly close in temperature, are shown in Fig. 11. The resultant DTG curves produced, when the two reactions are competing, are shown in Fig. 12. It will be noted that the combined DTG peak appears more like a first-order reaction peak. Indeed, although the diffusion-type DTG curve commences before that of the first-order DTG curve, the initial rate of this latter reaction is greater than that of the diffusion equation and, therefore, produces the dominant DTG curve. Obviously, the final shape of the resultant DTG curve will be highly dependent on the relative temperature positions of the two initial reactions.

6. Immediate reaction by the product of a reaction

One can envisage a situation where, as soon as the product of a reaction is formed it immediately reacts

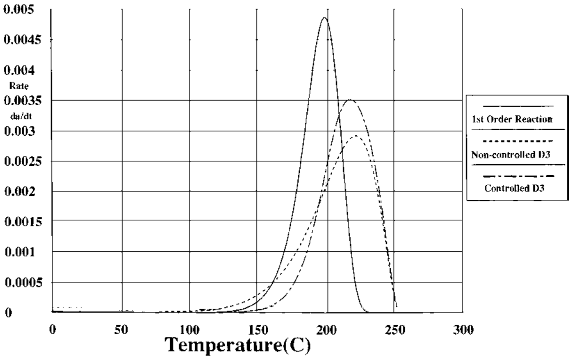

Fig. 13. Shift of DTG peak of a diffusion reaction when controlled by a first-order reaction.

again. Equations for such an arrangement are:

$$\mathrm{A} \rightarrow \mathrm{B} + C \uparrow$$

followed immediately by

$$\mathrm{B} \rightarrow \mathrm{D} + E \uparrow$$

For a single reaction, the total fraction reacted will be one and the rate of reaction will be governed by the reaction mechanism equation alone. However, if the product B commences to react as soon as product B is formed then the formation of a second product D will depend on two conditions: the reaction equation governing the second reaction to form the second product D and the amount of the first product B present at any given time. It is difficult to establish such a relationship, but the curves (Figs. 13 and 14) are based on the following relationships:

The first reaction is assumed to be a first-order reaction:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A_1(1-\alpha)\exp\left(-\frac{E_1}{RT}\right)$$

The second reaction is assumed to be a diffusion reaction (D3):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{3A_2\exp(-E_2/RT)}{2((1-\delta)^{-2/3}-(1-\delta)^{-1/3})}$$

Now the amount of β formed will depend on the amount of α present, so that the amount of β formed at any time can be written as:

$$\frac{\mathrm{d}\beta}{\mathrm{d}t} = \frac{\alpha(3A_2\exp(-E_2/RT))}{2((1-\beta)^{-2/3}-(1-\beta)^{-1/3})}$$

Note the presence of the fraction α of the first-order reaction in the diffusion equation. In Fig. 13, the three curves are the first-order DTG curve, an independent diffusion DTG curve and a diffusion curve controlled by the fraction reacted from the first reaction, both of the latter curves using the same values of E_2 and A_2. The uniform dotted DTG curve is that for the independent diffusion equation and the non-uniform dotted curve that of the same diffusion equation controlled by the product formation from the first-order equation.

A more realistic connection between two such reactions needs to be established in order to produce DTG and ln plots which compare with practical results, but the curves of Fig. 13 give some indication of what might be expected. The interesting finding from this reaction sequence is that the log plot for the second reaction, controlled as it is by the first reaction, is linear and gives a value of $E=-290.7$ kJ/mol for the reaction which is far greater than the value used in the theoretical calculations when $E=152.43$ kJ/mol. Thus, in a practical experiment, it would not be obvious from the DTG curve that the second reaction was the consequence of the first reaction and, furthermore, the activation energy derived from the DTG data would be incorrect. In practice, the peak obtained would be the resultant of the two separate DTG curves.

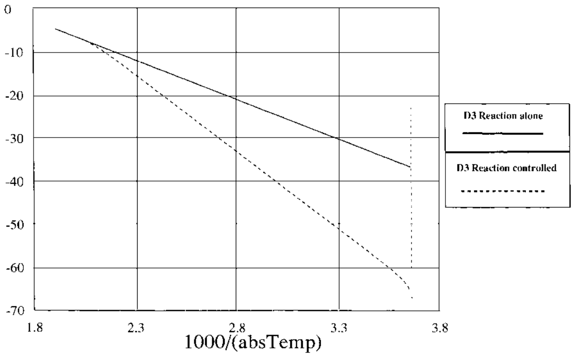

Fig. 14. Log plots for the diffusion reaction alone and when controlled by a first-order reaction.

7. Resolution of overlapping peaks

It has been claimed [12] that overlapping DTG or DTA peaks can be separated by carrying out experiments at different heating rates. Some of the heating rates suggested in that paper are not easily achievable,

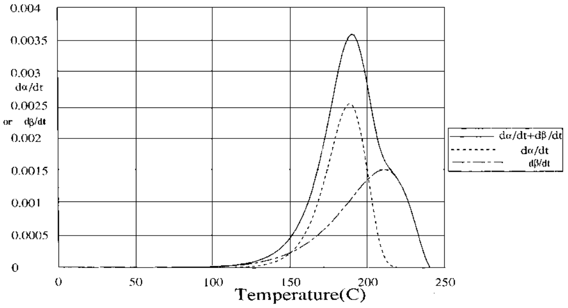

Fig. 15. Shift of multiple peaks at 5°C min.

for the experiments would be untimely long (of the order of days) or short (of the order of seconds). Separation was possible in some of the examples given in that paper, but the actual movement of the DTG or DTA peak for different heating rates is highly dependent on the values of *A* and *E* in the reaction equations. This effect is shown in Figs. 15–17 for different rates of heating. Note that the use of practical heating rates have not resolved the two peaks. Whether or not separation is achieved depends to a large extent on the values of activation energy and frequency factors for the individual reactions, as well as the type of reaction.

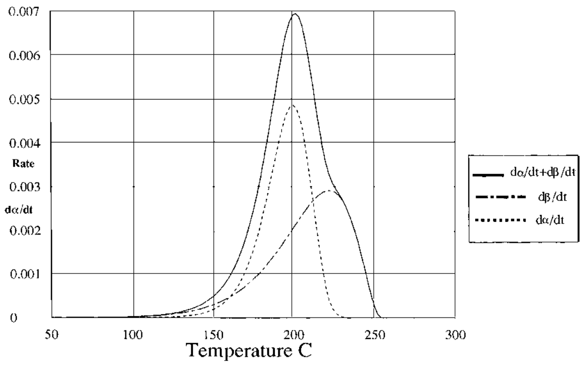

Fig. 16. Shift of multiple peaks at 10°C/min.

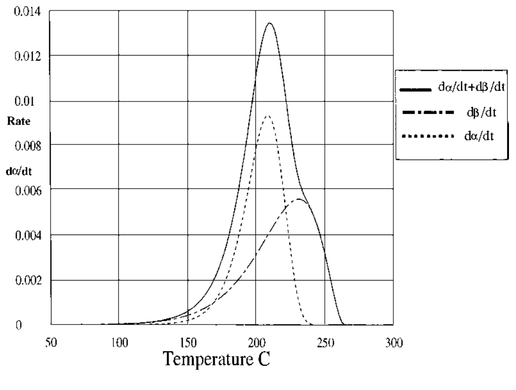

Fig. 17. Shift of multiple peaks at 15°C/min.

8. Conclusions

When two (or more) DTG peaks of equal height are clearly visible on a trace, the log plot usually consists of two (or more) straight lines connected by curves (Fig. 3). In such a situation, it is relatively easy to identify the separate log plots and, possibly, be able to measure the slope of each portion in order to calculate the *E* value for each individual reaction.

If, however, the peaks are close together or are overlapping and of differing heights due to fairly large differences in *E* or *A* values, then the compound log plot can be curved making it impossible to define the slope of this curve and, hence, to calculate the *E* and ln *A* values associated with each reaction.The practice of constructing 'the best straight line' is quite meaningless in this situation and is not to be recommended.Reactions which interact with each other often produce log plots which, although linear, do not give the true value of the activation energy associated with the reactions involved.

References

[1] J.G. Dunn, J.H. Sharp, in: J.A. Winefordner (Ed.),Treatise on Analytical Chemistry, Part 1, vol. 13, 2nd Edition. Wiley, New York, 1993.
[2] J.H. Sharp, G.W. Brindley, B.N. Narahari Achar, J. Am.. Ceram. Soc. 49 (1966) 379.
[3] F.W. Wilburn, J.H. Sharp, J. Thermal Anal. 41 (1994) 483.
[4] J. Malik, Thermochim. Acta 222 (1993) 105.
[5] H.E. Kissinger, J. Res. Nat. Bur. Stand. 57 (1956) 217.
[6] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[7] D. Dollimore, T.A. Evans, Y.F. Lee, G.P. Pee, F.W Wilburn, Thermochim. Acta 196 (1992) 255.
[8] A. Savitzky, M.J.E. Golay, Anal. Chem. 36 (1964) 1627.
[9] J. Steiner, Y. Termonia, J. Deltour, Anal. Chem. 44 (1972) 1906.
[10] H.H. Madden, Anal. Chem. 50 (1978) 1383.
[11] T.A. Evans, Y.F. Lee, D. Dollimore, F.W. Wilburn, Thermochim. Acta. 188 (1991) 77.
[12] J.H. Flynn, Thermochim. Acta 37 (1980) 225.