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NEW METHOD FOR TG AND DSC DATA ANALYSIS

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ABSTRACT

The paper describes a graphical computer method for analysing TG and DSC traces which gives all three reaction parameters (E, A, and n) characterising an nth-order reaction from a single trace. If the reaction proceeds in multiple stages (E, A and n) triplets can be obtained for each stage. The computer programmes are basically simple and use little computing time (typically a few seconds). The advantages of the approach over earlier methods are discussed. As a test of the method, results on the dehydration of calcium oxalate monohydrate are described.

INTRODUCTION

The deduction of the reaction parameters E (activation energy), A (frequency factor), and n (reaction order) from TG, and DSC traces is clearly of interest. A number of methods have been used in the past to do this but all have unsatisfactory features. In the work described here a number of Fortran programmes were written to extract all three reaction parameters of an nth-order reaction from a single TG, or DSC trace. The programmes were run on the Cambridge IBM 370/165 computer, and the plotter was used for graphical output. So that the advantages of the present approach can be appreciated earlier methods are briefly discussed.

EARLIER METHODS

Murray and White[1] have shown that the temperature at the reaction peak of DTA traces can be used to obtain E and A from a number of traces if a first order reaction (eqn. 1) is assumed, where w is the fractional residual weight, t the time, T the temperature and R the gas constant.

$$\frac{dw}{dt} = -A \exp\left(-\frac{E}{RT}\right) w \tag{1}$$

If eqn. (1) is differentiated to obtain the maximum for dw/dt then eqn. (2) can be derived, where $\phi = dT/dt$ is the heating rate and T_m the temperature at the rate maximum.

$$\ln\left(\frac{\phi}{T_m^2}\right) = \ln\frac{AR}{E} - \frac{E}{R}\frac{1}{T_m} \tag{2}$$

A plot of $1/T_m$ versus $\ln(\phi/T_m^2)$ yields E/R as the slope and $\ln(AR/E)$ as the intercept of the straight line with the ordinate. The main disadvantage of this method is that it only uses a single point (T_m) from a trace to produce one point on the activation energy plot. A number of experiments are needed to obtain a reliable value for E. There is also the limitation that the theory only works for a first-order reaction.

Kissinger[2] showed that the technique can be extended to an nth-order reaction by deriving eqn. (3).

$$\frac{E}{RT_m^2} = A\, n\, w_m^{n-1} \exp\left(-\frac{E}{RT_m}\right) \tag{3}$$

He shows in his paper that the product $n\, w_m^{n-1}$ is independent of the heating rate (ϕ) and almost equal to unity. Therefore, eqn. (3) effectively reduces to eqn. (2). The approach again makes poor use of the information contained in a DTA trace.

Ozawa's analysis[3] of TG traces begins with a general form of reaction equation.

$$\frac{dw}{dt} = -A\exp\left(-\frac{E}{RT}\right) f(w) \tag{4}$$

This is integrated by Ozawa who shows that the solution to the right-hand side of the equation is a polynomial in the variable E/RT. Equation (5) is an approximate formula which relates the heating rate ϕ with E.

$$\log\phi_1 + 0.4567\frac{E}{RT_1} = \log\phi_2 + 0.4567\frac{E}{RT_2} \tag{5}$$

where T_1 and T_2 correspond to the same fractional decomposition (w) of the sample. Since a plot of $\log\phi$ versus $1/T$ can be obtained for each value of w, Ozawa aggregates all these results in a master-curve with a gain in accuracy of the final result. Equation (5) only assumes that the function $f(w)$ is constant for a given value of w.

This method also needs a number of experiments at different heating rates to generate enough data for a single activation energy plot. Although the method was developed for thermogravimetric data, it can be applied to DSC data by integrating the peaks to give values of w. A theoretical analysis of such a process is given by Reed et al.[4].

Borchardt and Daniels[5] describe a method which allows E, A and n to be determined from the shape of a DTA curve. Their approach was applied to reactions in the liquid phase. The type of reaction to which this method is applicable must have a single rate constant and the activation energy must not vary with temperature. By considering the heat transfer equation of the calorimeter eqn. (6) was obtained

$$-\frac{dN}{dt} = \frac{N_0}{KA'}\left\{C_p\frac{d\Delta T}{dt} + K\Delta T\right\} \tag{6}$$

where N is the number of moles present, N_0 the initial number, K the heat transfer coefficient, A' the area under the DTA curve, C_p the heat capacities of the two liquids and ΔT the temperature difference between the two cells. Integration of eqn. (6) with respect to time gives

$$N = N_0 - \frac{N_0}{KA'}\{C_p \Delta T + Ka\} \tag{7}$$

where a is the area under the DTA curve up to the present temperature.

The expression for the rate constant k of a reaction of order n is

$$k = -V^{(n-1)}\frac{\mathrm{d}N/\mathrm{d}t}{N^n} \tag{8}$$

where V is the volume. Substituting eqns. (6) and (7) for dN/dt and N gives

$$k = \left\{\frac{KA'V}{N_0}\right\}^{n-1}\frac{C_p\frac{\mathrm{d}\Delta T}{\mathrm{d}t} + K\Delta T}{\{K(A'-a) - C_p\Delta T\}^n} \tag{9}$$

In order to obtain reaction parameters, Borchardt and Daniels[5] assumed a value for n. This allowed k to be calculated. A plot of ln k versus $1/T$ (activation energy plot) yields a straight line if, and only if, the correct value of n has been assumed, thus values of E, A and n can be obtained. The main difficulty of this method is the number of plots that have to be made for each value of n until the points lie on a straight line.

A number of computer programmes are presented by Benin et al.[6] and used to solve three problems, namely (i) the production of thermograms given the reaction parameters E, A, n and given that the reaction is of the nth-order type; (ii) the calculation of the (E, A, n) triplet from an experimental thermogram — this is the inverse to problem (i); and (iii) the determination of the reaction parameters and the complex reaction mechanism from a given experimental thermogram. The first problem is a straightforward function plot of the solution to the nth-order reaction equation. The second problem is more difficult, and presents itself to anyone who wants to obtain reaction parameters from experimental data. Benin et al.[6] treat it as a problem in curve fitting. They minimise the discrepancy between the experimental data and the calculated function by taking as the discrepancy criterion the maximum deviation of the function from the data. The solution of the third problem is an attempt to reveal the mechanism of a chemical reaction. The programmes become quite involved as they work out activation energies for each section of the thermogram by using a plot of reaction rate versus $1/T$ for a constant amount of conversion, x, but different heating rates.

The most general form of the fit function assumes a decomposition process which proceeds in a number of individual stages. Each stage consists of an elementary nth-order reaction, i.e., eqn. (1) with A, E and w replaced by A_i, E_i and w_i, respectively, where "i" denotes the variable belonging to the ith stage of the reaction. The programme which optimises the fit of this function to the data takes up to 4 h of computing time. This makes the method rather expensive. Another weak point is the discrepancy criteria between the data and the fit, which is taken as the maximum difference. It is well known that the data points towards the end of a decomposition process become less reliable due to impurities and zero errors. But these points have the same weight in the analysis as all the others.

Schempf et al.[7] describe a programme which fits a least square polynomial to the weight-loss curve. The quantity dw/dt is calculated by differentiation of the polynomial. A straight line is then fitted to a plot of log k versus $1/T$, and the least square criterion is used again. The reaction order is assumed to be one, and no attempt is made to eliminate the deviations from an ideal reaction at the beginning and end of the weight-loss curve. Our work shows that this is very critical and can be obtained from an Arrhenius plot performed by the computer.

NEW METHOD

The method developed was based on the ideas of Borchardt and Daniels[5]. Our data were obtained from both a thermobalance (Stanton Redcroft) and a differential thermal calorimeter (Perkin-Elmer DSC-2).

The analysis assumes a reaction which can be described by

$$\frac{dw}{dt} = -A_i \exp\left(-\frac{E_i}{RT}\right) f_i(w) \tag{10}$$

Since the heating rate h (deg min^{-1}) is constant, the time variable can be eliminated from eqn. (10) by putting $dT/dt = h/60$ (deg sec^{-1}).

Taking natural logarithms on both sides gives

$$\ln\left(-\frac{dw_i}{dt}\right) - \ln f_i(w) = \ln\frac{A_i \times 60}{h} - \frac{E_i}{RT} \tag{11}$$

Note that $(-dw/dt)$ is a positive quantity since the fractional residual weight decreases with increasing temperature.

A plot of $\{\ln(-dw_i/dt) - \ln f_i(w)\}$ versus $\{1/T\}$ only yields a straight line if $f_i(w)$ has been chosen correctly. In the case of $f_i(w) = w^n$ the reaction order n is varied until a straight line is found. The activation energy E can be obtained from the slope of this plot, the frequency factor A from the intercept on the ordinate and the reaction order n is determined by the straight line criterion.

This analysis can also be applied to the DSC data since the basic eqn. (12) only differs from (10) by constants.

$$\frac{dQ}{dt} = \pm \Delta H(w_0 - w_t)\, A \exp\left(-\frac{E}{RT}\right) f(w) \tag{12}$$

The + (−) in the equation corresponds to an exothermic (endothermic) reaction where, Q is the heat given off by the sample, ΔH is the enthalpy change of the entire reaction, w_0 is the initial weight and w_r is the rest weight, and the other parameters are as defined previously.

Taking logarithms gives

$$\ln\left(\frac{dQ}{dt}\right) - \ln f(w) = \ln \Delta H(w_o - w_r) A - \frac{E}{RT} \tag{13}$$

This time dQ/dt at temperature T is the measured quantity and w needs to be calculated. This is easily done since, if the reaction results in a weight loss

$$w_t = \frac{1}{\Delta H}\int_0^t \frac{dQ}{dt}\,dt \tag{14}$$

The computer numerically integrates dQ/dt to yield the weight at time t. A plot of $\{\ln dQ/dt - \ln f(w)\}$ versus $1/T$ produces E, A and n (if $f(w) = w^n$) in the same way as for the weight-loss curves above. The slope is again $-E/R$ and the intercept is $\ln \Delta H(w_0 - w_r)A$.

In practice the data from the TG or DSC is recorded on 8 track ASCI paper tape. This information is then read into disc files of the computer. These files can be used by the programmes which calculate the activation energy, etc. After these programmes have run, the plotter output is viewed on a television screen. Only if the plot is satisfactory is a copy obtained from the plotter for the final analysis. The dimensions correspond to the original output of the chart recorder so that a direct comparison is possible. Different pen colours are used to differentiate between the raw data (black) and the theoretical fit to the data (green). These colours are represented in Fig. 1 as a broken line (black) and a full line (green).

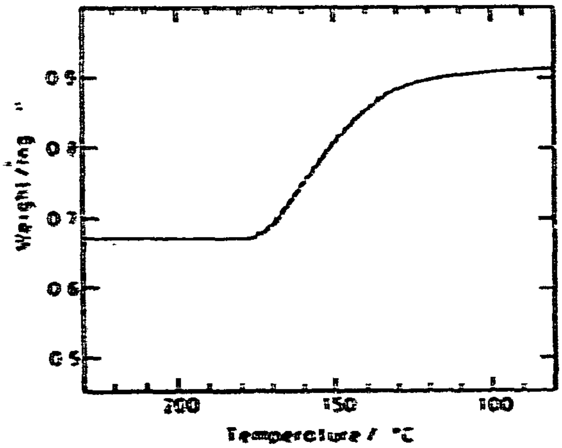

Fig. 1. Weight loss curve of Ca $C_2O_4H_2O$ analysis. The dashed line is the original data and the full line the replot using the computed (E, A, n) triplet for the three straight line sections which are separated by vertical dashed lines.

The differential programme[*]

There are three different ways in which differentials to the weight-loss curve were obtained. The first uses differences and produces a noisy differential curve, which is, however, nearest to the original data. The other two use a polynomial fit, and a spline fit, respectively. The polynomial fit, usually of 25th order, is generally good but produces artificially large undulations over straight regions of the curve. The best results were obtained by a cubic spline fit. This programme fits a third order curve to sections of the data, and joins them in such a way that the function and the first two derivatives are continuous. The programme uses a standard subroutine from the Harwell Fortran library, which chooses its own knots (points where two splines meet) according to the behaviour of the original curve. This means that over a straight part of the curve a long section can be fitted by a single cubic spline, whereas at places of greater variation, smaller sections are chosen to be approximated. The differential of the curve is then obtained by differentiating the third order spline. The fit of the spline and the differential is very accurate. The amount of data smoothing achieved by this fit suits the purpose of the following programme (next section) best.

The programme to find E, A and n

It is assumed in this analysis that the reaction that leads to the weight-loss curve is at least piece-wise of the nth order, i.e. follows eqn. (10) with $f_i(w) = w^n$. This programme plots $\{\ln(-dw/dt) - n \ln w\}$ versus $1/T$ for different values of n. The values of dw/dt and of w are obtained from a file that was created by the previous programme and contains the smoothed weight-loss data and the differential in the form of the spline parameters. The value of n is taken as zero for the first plot and then increased by 0.2 ten times up to $n = 2$. These eleven lines have different curvatures. The straightest of them can easily be selected by eye and this n value is then taken as the reaction order. The slope yields E and the intercept A. The resulting triplet of numbers (E, A, n) are necessary and sufficient to characterise an nth-order reaction. The type of reaction, i.e. $f(w) = w^n$ can be changed easily so that the programme is applicable to reactions of any type, i.e. $f(w)$ can have any form (e.g. random chain scission).

The programme to produce a theoretical fit from the (E, A, n) triplet

This programme allows the production of a weight-loss curve with up to four different sections each of which has its own E, A and n factor. It was implemented on a Hewlitt Packard Desk top calculator and plotter of the type HP 9825. The theoretical plots produced in such a way fit the original weight-loss curve very well. They also provide a useful check that all the calculations necessary to produce this triplet were correct, and produce a good fit.

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[*] This and the following programmes can be obtained from the authors.

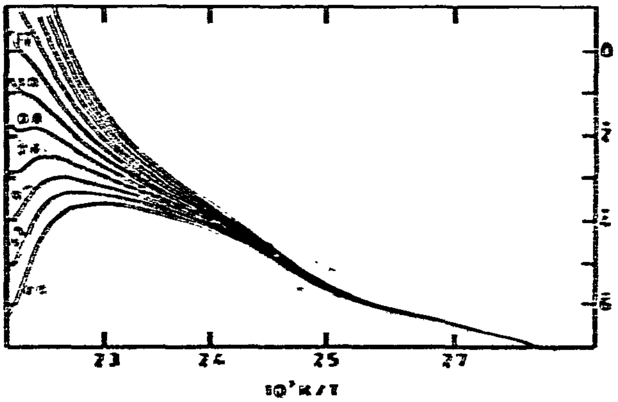

Fig. 2. Activation energy plot for various values of reaction order *n*. The *n* value which gives the best straight line segments is the one appropriate to the reaction (here 0.6). There are three steps to the reaction but the first two correspond to only ca. 2% of the weight-loss.

TEST OF METHOD

The dehydration reaction of calcium oxalate monohydrate

$$Ca\ C_2O_4H_2O \rightarrow Ca\ C_2O_4 + H_2O$$

is well understood and values for the reaction parameters can be obtained from the literature[8, 9]. It therefore provides a good test case for the new analysis method. Figure 1 shows the weight-loss curve of a sample of Ca $C_2O_4H_2O$. The dashed curve represents the original data and the full curve the theoretical fit based on the computed (*E*, *A*, *n*) triplet. Figure 2 shows the activation energy plot. The number at the end of each line gives the reaction order that is assumed for the calculation of the corresponding line. The straight lines which approximate the curves best are used to obtain (*E*, *A*, *n*) triplets for the three sections. Since these (*E*, *A*, *n*) triplets completely specify the reaction the original weight-loss curve can be modelled (full curve Fig. 1). The results obtained with this method, and literature values are summarized in Table 1. All our experiments were performed at a heating rate of 10 deg min^{-1}. The results obtained in this way have an error of ± 5 kJ mol^{-1} which is due to the variance of the samples themselves. The method itself has much greater accuracy. It was found that the best straight line could be fitted to a curve corresponding to a reaction order of 0.6

TABLE 1

E (*kJ mole*$^{-1}$)	*ln A*	*Ref.*
87	19.8	This work
84	17.5	This work
88	21.0	8
92		9

which indicates a surface reaction (theoretically 2/3). It can also be seen on Fig. 2 that there are three distinct stages of the reaction. The first two, however, correspond to only 2% of the weight and are attributed to volatile substances on the surface. This shows the sensitivity of the method used especially considering that the vertical axis has a logarithmic scale. The real dehydration reaction is represented by the last straight line segment.

The method outlined in this paper has recently been successfully applied[10] to decomposition studies of P.E.T.N., P.E.T.N. with fillers, high density polyethylene (HDPE) and polytetrafluoroethylene (PTFE).

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