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The evaluation of kinetic parameters from thermogravimetric curves

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Abstract

The evaluation of kinetic parameters from thermogravimetric curves is considered for two linear transformations of the rate expression for various decomposition models. The differentials are calculated by applying splines to theoretically calculated curves for ten decomposition models and to an experimental curve for the decomposition of magnesite. The sensitivity of the values of the kinetic parameters with decomposition model obtained for the two treatments are investigated and, in the case of the experimental data, compared with values obtained for the integral treatment of the rate equation.

INTRODUCTION

The methods of obtaining kinetic parameters from non-isothermal data using linear transformations of the rate equation and its differential form are well established [1]. The main source of error occurs in the determination of the derivative terms $d\alpha/dT$ and $d^2\alpha/dT^2$ from the thermogravimetric curves. This paper considers calculation of kinetic parameters using two forms of the differential equation and shows that the derivative terms may be conveniently expressed by spline functions. It also considers the sensitivity of the two treatments to the decomposition model for theoretically calculated data and for experimental data.

EXPERIMENTAL

TG curves were measured with a Stanton–Redcroft TG760 instrument using a Metrobyte Dash-8 analog-to-digital converter or a voltage-to-frequency converter interfaced to an IBM-XT computer. Data collection

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

and analysis were performed using software written with TURBO-PASCAL (Version 5).

RESULTS AND DISCUSSION

Second-differential method

The expression for the first method is obtained from the basic rate equation

$$d\alpha/dT = Ag(\alpha)\exp(-E/RT)/b \quad (1)$$

where A is the pre-exponential constant, E is the activation energy, b is the heating rate and the function $g(\alpha)$ is the differential form for the decomposition model tabulated in Comprehensive Chemical Kinetics, Vol. 22 [1]. Differentiation with respect to temperature and manipulation leads to the expression

$$\frac{d^2\alpha/dT}{d\alpha/dT} - \frac{dg(\alpha)/dT}{g(\alpha)} = \frac{E}{RT^2} \quad (2)$$

The TG curves may be simply transformed to α/T curves, and the derivative terms $d\alpha/dT$ and $d^2\alpha/dT^2$ may be expressed by applying a spline function, using computer programs given in Numerical Recipes [2]. A straight line graph with gradient E/R and zero intercept results when the left-hand side of the expression is plotted against $1/T^2$ for the correct model, and a value of the pre-exponential constant may be obtained by back-substitution in the original equation. Theoretical TG curves were calculated for ten decomposition models (F1, F2, A2, A3, D1, D2, D3, D4, R2 and R3) by integrating the rate equation using numerical predictor-corrector methods [3]. Values of the kinetic parameters were kept constant throughout, with a pre-exponential constant $A = 2.0 \times 10^{10}$ min^{-1}, an activation energy of 185 kJ mol^{-1} and a heating rate $b = 10$°C min^{-1}. The spline treatment was applied to the ten theoretical curves, and the results analysed by linear least-squares methods for each of the ten decomposition models.

Table 1 shows some of the models with the best fits and gives values and errors for the intercept and the activation energy obtained from the gradient. In some cases, it shows that the theoretical data may be fitted by several models, which have been previously observed [4,5] for the groupings of F1, A2 and A3 models, and D3 and R3 models. Despite these groupings having comparable values of χ^2, unambiguous model identification may be made on the basis of the zero intercept.

Some treatment of experimental data was necessary because of the sensitivity to noise of the second-derivative term in the spline treatment.

TABLE 1

Second-differential analysis of calculated TG curves

Input model	Analysis model	10^6 Intercept	E (kJ mol^{-1})	χ^2
F1	F1	−14± 3	185.0±0.02	1.6×10^{-9}
	A2	541± 3	88.9±0.02	1.5×10^{-9}
	A3	−717± 3	56.8±0.02	1.5×10^{-9}
F2	F2	7± 4	184.9±0.03	2.0×10^{-9}
A2	F1	1130± 12	376.6±0.07	3.1×10^{-8}
	A2	7± 11	184.8±0.02	2.4×10^{-8}
	A3	−368± 10	120.9±0.02	2.2×10^{-8}
A3	F1	5615±314	546.8±0.79	3.7×10^{-6}
	A2	1517± 40	184.9±0.01	3.3×10^{-7}
	A3	151± 22	274.6±0.24	9.9×10^{-8}
D1	D1	3± 2	183.9±0.13	1.3×10^{-9}
D2	D2	19± 3	184.8±0.02	1.9×10^{-9}
D3	D3	−4± 3	184.9±0.02	1.5×10^{-9}
	R3	−574± 3	89.1±0.01	1.4×10^{-9}
D4	D4	16± 3	184.8±0.01	1.5×10^{-9}
R2	R2	33± 3	184.7±0.02	5.1×10^{-9}
R3	R3	−12± 5	377.0±0.04	1.4×10^{-9}
	D3	14± 3	185.0±0.03	1.5×10^{-9}

Data measured with the voltage-to-frequency converter were superior to those measured by numerical averaging, but smoothing by the Savitsky–Goulay method was still required.

Although, from a theoretical standpoint, the technique of zero intercept appears to offer a quick unambiguous way of determining appropriate kinetic models, in practice, this will not be the case. The problem stems from the determination of the second derivative and its sensitivity to noise in the experimental α/T curve. In all but the best of experimental data, the noise present in the α/T curve will give rise to a poorly determined second derivative, and unacceptably high confidence levels for the intercept, making the choice of model a difficult task.

The noise problem for experimental data is evident in Fig. 1, which shows the $d^2\alpha/dT^2$ vs. T curve obtained from the spline treatment, where it is apparent that large fluctuations in the second derivative exist around the critical 930 K region. This was overcome by curtailing the data to cover the range of $\alpha = 0.02$–0.75, and by applying various levels of Savitsky–Goulay smoothing.

These problems are also demonstrated in Table 2, which shows the sum-of-the-squares of the residuals χ^2, and values with errors for the intercept and the activation energy E obtained by applying the spline treatment for each of the ten decomposition models to the 27-point smoothed experimental data.

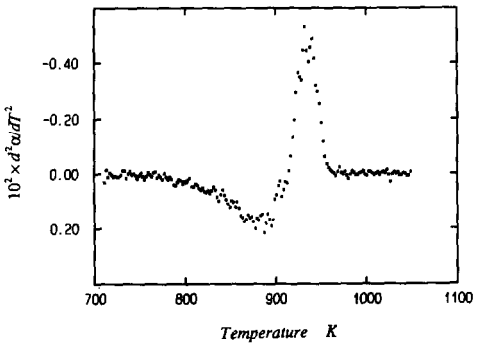

Fig. 1. Spline values of $d^2\alpha/dT^2$ calculated from the TG curve for < 75 μm magnesite in nitrogen heated at 30°C min^{-1}.

The discrimination between different models is certainly not as clear cut as it is for theoretically calculated curves, but the R3 contracting-core model may be selected out of the possible D3, R2 and R3 models on the basis of the value of the intercept and the residuals. Some of the other models could be dismissed on the grounds of negative activation energies and non-zero intercepts. Figure 2, which is a plot of the left-hand side of eqn. (1) against $1/T^2$, makes it apparent why there is such a large spread in the values calculated for E. The straight line is the least-squares fit, which should, in theory, pass through zero if the correct model has been selected.

Differential method

The second method uses the logarithmic form of the basic rate equation

$$\ln\left(\frac{d\alpha/dT}{g(\alpha)}\right) = \ln\left(\frac{A}{b}\right) - \frac{E}{RT} \tag{3}$$

TABLE 2

Differential analysis of smoothed experimental TG curve

Analysis model	Intercept 10^3	A (min^{-1})	E (kJ mol^{-1})	χ^2 $\times 10^3$
F1	70± 8	–	–	1.2
F2	243±19	–	–	7.1
A2	47± 7	–	–	1.0
A3	40± 7	–	–	8.95
D1	−127±13	(1.0± 0.3)×10^{16}	1030.6±73.8	3.1
D2	−57± 9	(4.1± 0.3)×10^{17}	648.4±52.1	1.6
D3	31± 6	(2.5± 5.6)×10^{18}	165.9±35.8	0.74
D4	−26± 7	(4.3±65.0)×10^{17}	480.7±42.8	1.1
R2	−16± 6	(1.0± 4.1)×10^{18}	256.2±36.6	0.77
R3	13± 6	(2.3± 3.8)×10^{18}	98.8±35.2	0.71

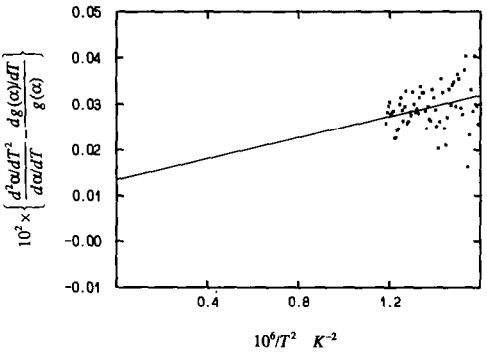

Fig. 2. Linear plot of second-differential method.

where the kinetic parameters are as defined for eqn. (1). The differential term $d\alpha/dT$ may be rapidly obtained by applying a spline function to the transformed TG curve. A straight line graph with gradient $-E/R$ and intercept $\ln(A/b)$ results for the correct model when the left-hand side of the expression is plotted against $1/T$. The spline treatment [2] was applied to the ten theoretical curves, and the results analysed by linear least-squares methods for each of the ten decomposition models.

Some idea of the sensitivity of the treatment to the decomposition model is seen in Table 3, which presents the best fit analyses for each model based on the lowest values of χ^2. Values of the kinetic parameters, A and

TABLE 3

Differential analysis of calculated TG curves

Input model	Analysis model	A (min^{-1})	E (kJ mol^{-1})	χ^2
F1	F1	2.0×10^{10}	184.9 ± 0.0	2.5×10^{-13}
	A2	1.5×10^{4}	184.9 ± 0.0	1.8×10^{-5}
	A3	1.1×10^{2}	52.2 ± 0.0	3.2×10^{-5}
F2	F2	2.0×10^{10}	184.9 ± 0.0	1.8×10^{-16}
A2	F1	1.7×10^{22}	383.5 ± 0.0	8.7×10^{-5}
	A2	2.0×10^{10}	184.9 ± 0.0	2.8×10^{-12}
	A3	1.8×10^{6}	118.7 ± 0.0	9.6×10^{-6}
A3	F1	9.6×10^{33}	581.3 ± 0.1	1.2×10^{-3}
	A2	1.9×10^{16}	283.8 ± 0.0	7.5×10^{-5}
	A3	2.0×10^{10}	184.9 ± 0.0	2.4×10^{-11}
D1	D1	2.0×10^{10}	184.9 ± 0.0	3.2×10^{-17}
D2	D2	2.0×10^{10}	184.8 ± 0.0	3.2×10^{-14}
D3	D3	2.0×10^{10}	184.9 ± 0.0	3.6×10^{-15}
	R3	3.9×10^{4}	85.8 ± 0.0	2.4×10^{-5}
D4	D4	2.0×10^{10}	184.9 ± 0.0	1.3×10^{-14}
R2	R2	2.0×10^{10}	184.9 ± 0.0	1.1×10^{-14}
R3	D3	2.9×10^{21}	383.6 ± 0.0	8.2×10^{-5}
	R3	2.0×10^{10}	184.9 ± 0.0	3.2×10^{-13}

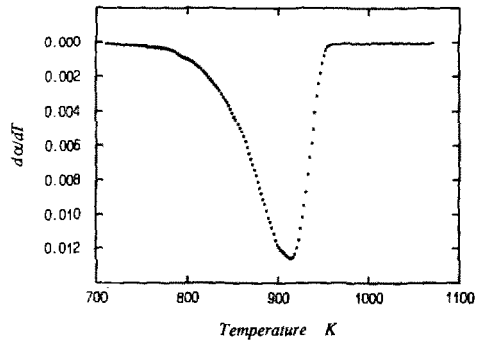

Fig. 3. Spline values of $d\alpha/dT$ calculated from the TG curve for < 75 μm magnesite in nitrogen heated at 30°C min^{-1}.

E, and their errors are also given. The choice of model for theoretical data is unambiguous on the basis of the minimum residuals, and the same groupings of models are observed [4,5] with the following relationships between the activation energies: $E(F_1) = 2E(A_2) = 3E(A_3)$; and $E(D_3) = 2E(R_3)$.

Fig. 3 shows that the spline calculation of the first derivative is less sensitive to experimental noise, and this is reflected in the errors for the kinetic parameters obtained from the spline treatment of the unsmoothed data given in Table 4. Again, discrimination between the possible models of decomposition is not as clear cut as for the theoretical data, and there is little difference in the range of the residuals for the ten models. Either the R2 or R3 model could be chosen on the basis of the minimum sum of the residuals. Figure 4 shows the straight line plot for the R3 model.

The values for the kinetic parameters, $A = 5.4 \times 10^{10}$ min^{-1} and $E = 180$ kJ mol^{-1}, may be compared with the previously [6] obtained values of

TABLE 4

Differential analysis of unsmoothed experimental TG curve

Analysis model	A (min^{-1})	E (kJ mol^{-1})	χ^2
F1	$(6.6 \pm 3.4) \times 10^{10}$	196.9 ± 5.1	3.9
F2	$(1.2 \pm 0.8) \times 10^{14}$	247.7 ± 7.2	7.6
A2	$(1.2 \pm 0.6) \times 10^{5}$	101.9 ± 4.9	3.6
A3	$(1.2 \pm 0.6) \times 10^{3}$	70.2 ± 4.9	3.6
D1	$(9.2 \pm 4.3) \times 10^{14}$	312.5 ± 5.5	4.4
D2	$(2.9 \pm 1.4) \times 10^{18}$	335.9 ± 5.0	3.7
D3	$(4.2 \pm 2.1) \times 10^{19}$	361.6 ± 5.0	3.7
D4	$(3.5 \pm 1.8) \times 10^{18}$	344.6 ± 4.9	3.6
R2	$(1.5 \pm 0.8) \times 10^{9}$	171.4 ± 4.9	3.5
R3	$(5.4 \pm 2.7) \times 10^{10}$	179.9 ± 4.9	3.5

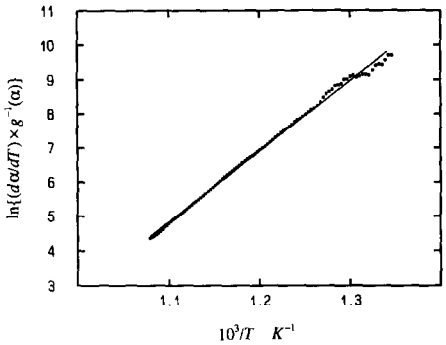

Fig. 4. Linear plot of differential method.

$A = 4.8 \times 10^{11}$ min^{-1} and $E = 174$ kJ mol^{-1} using the integral predictor-corrector method for the R3 model, for which the experimental and calculated α/T and $d\alpha/dT$ curves are shown in Fig. 5. The effect of using 15-point Savitsky–Goulay smoothing greatly reduces the sum of the residuals from 3.5 to 0.16, but has little effect on the magnitude of the parameters, with the value of A remaining unaltered and E becoming 178 kJ mol^{-1}.

CONCLUSIONS

Values of kinetic parameters may be rapidly obtained from linear treatments of two forms of the rate equation using a spline treatment of experimental TG curves.

The method using the differential form of the rate equation is more sensitive to noise and round-off error. Not only is this evident in experimental data for small mass changes at the initial and final stages of the reaction, but also at the turning points of the second-derivative curve. This

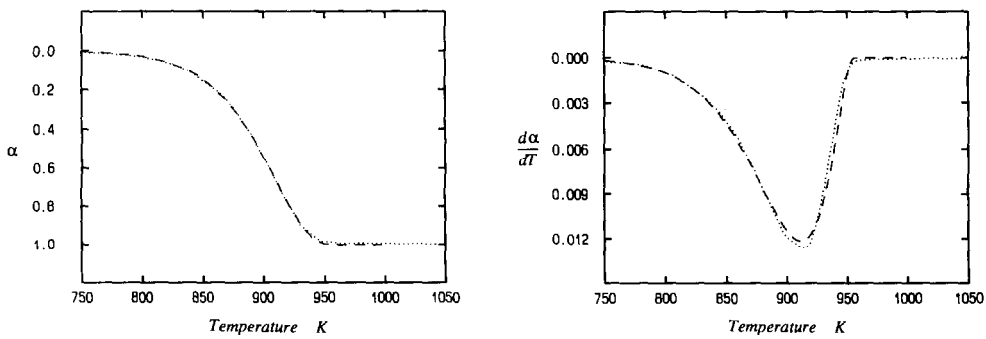

Fig. 5. Experimental (broken) and calculated (dotted) α/T and $d\alpha/dT$ curves for < 75 μm magnesite in nitrogen heated at 30°C min^{-1}.

limits the range of α over which the model may be used, and often neglects the important data obtainable from the start and finish of the TG curve. With smoothing, however, discrimination between the various models is possible on the basis of the zero intercept, but little confidence can be placed on the value for the activation energy.

The method based on the rate equation is much less sensitive to data noise, and selection of decomposition model can be made on the basis of the minimum value of the residuals. The method also gives smaller errors for the kinetic parameters, which are in good agreement with previously obtained values. The use of voltage-to-frequency converter data with lower noise should improve the value of both these methods.

By using spline functions to represent thermogravimetric curves, one can use the mathematical expressions given in eqns. (2) and (3) as written, without recourse to graphical methods of analysis. In so doing, it is possible to analyse the experimental data in such a way that many of the sources of error, which are encountered in other methods, may be avoided and more reliable estimates of the confidence limits for the kinetic parameters may be obtained. For the case of the second-differential method, it is now possible to examine the behaviour of the second derivative, the major source of error, in some detail and determine the suitability of the experimental data for this type of analysis. Where it is obvious that the experimental data are far too noisy, giving rise to an ill-defined second derivative, it is then advisable to adopt an alternative approach rather than attempting to smooth extensively the original data.

The best strategy for the calculation of kinetic parameters would be to use the method based on the rate equation to identify the most likely models and to obtain values of A and E as the starting point for a predictor-corrector, non-linear least-squares analysis of the TG curve. This method has the advantage of using the important data obtainable from the start and finish of the TG curve, where large changes in shape occur with model selection. The use of better estimates for the values of the kinetic parameters will also reduce the number of cycles needed for convergence and minimize the computing time for the non-linear least-squares treatment.

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