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THE DISTINGUISHABILITY OF KINETIC MODELS USING A SINGLE, NON-ISOTHERMAL THERMAL ANALYSIS EXPERIMENT

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ABSTRACT

A critical analysis of the kinetic evaluation from a single non-isothermal experiment using the computerized method of Skvara and Sestak, is presented . Theoretical data with varying amounts of random errors has been used to test the reliability of such a procedure. This has shown that questionable results arise if experimental data of worse than ±2.5% error is used. The method has also been tested using experimental data for the degradation of polystyrene and a polyamide. Although we recommend this procedure for a quick, kinetic analysis from any thermal analysis technique, additional kinetic studies are necessary owing to the inherent shortcomings of non-isothermal kinetics and the vulnerability of the present method to small errors.

INTRODUCTION

It is often desirable to analyze thermal analysis data to obtain the activation energy, Arrhenius factor, and possible mechanism or order of reaction. This data, together with other information obtained from these studies, is very useful for a better evaluation of practical processes involving condensed phases. Examples of such studies have been reviewed previously [1].

The types of processes which can be studied include decomposition, curing, polymerization and sintering, etc. Frequently, kinetic studies are carried out using data from several isothermal experiments or from a series of rising temperature, i.e. non-isothermal experiments, using different heating rates [1]. However, many methods are available which only require data from a single, rising temperature experiment [2]. The aim of this work is to describe the development of a computer program using one of these methods. An analysis of the effects of experimental error is presented, using both theoretical and experimental data. This kind of evaluation of the method has not been described elsewhere, but is believed to be essential before kinetic parameters can be quoted with confidence.

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THEORETICAL BACKGROUND

In general, most methods of kinetic analysis for thermal analysis data begin from the Arrhenius equation

$$k = A \exp(-E/RT) \tag{1}$$

and a rate expression

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{2}$$

The first equation links the activation energy E and the specific rate constant k by the temperature T gas constant R and Arrhenius factor A. Equation (2) is analogous to formal kinetic expressions except that, instead of using concentration, the fraction converted α at time t is used. Thus experimental data must first be normalized between 0 and 1.

By substituting the heating rate $\beta = \mathrm{dT/dt}$ and solving eqns. (1) and (2) for k it can be shown that

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}\frac{\beta}{f(\alpha)} = A \exp(-E/RT) \tag{3}$$

The basis of the method described here is an integrated form of eqn. (3) [3–6], i.e.

$$\int_0^\alpha [1/f(\alpha)]\ \mathrm{d}\alpha = \int_0^T \frac{A}{\beta} \exp(-E/RT)\ \mathrm{d}T \tag{4}$$

The left-hand side of this equation is known as $g(\alpha)$, and can be derived for each $f(\alpha)$ used. In order to solve the right-hand side, however, it is necessary to substitute $x = E/RT$, and its associated derivative

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{-E}{Rx^2} \tag{5}$$

so giving

$$g(\alpha) = \frac{AE}{R\beta} p(x) \tag{6}$$

where $p(x) = -\int x^{-2} \exp(-x)\ \mathrm{d}x$, this being known as the temperature integral. The equation is normally quoted in its logarithmic form, i.e.

$$\ln g(\alpha) = \ln\left(\frac{AE}{R\beta}\right) + \ln p(x) \tag{7}$$

and is the basis of many so-called integral methods. In general, these methods are fairly sensitive to changes in mechanism, i.e. $g(\alpha)$, but are complicated by the temperature integral.

There are many series expansions for $p(x)$ and comparisons of these [7–9] have shown the following to be most accurate.

$$p(x) = \frac{\exp(-x)}{x(x+1)}\left(1 - \frac{1}{(x+2)} + \frac{1}{(x+2)(x+3)} + \cdots \frac{1}{(x+2)\ldots(x+n)}\right) \tag{8}$$

In practice this is normally used to a maximum of five terms.

Since ln $p(x)$ is a logarithm of an exponential function of temperature, then a plot of ln $p(x)$ versus $1/T$ will be linear. Thus, because $\ln(AE/\beta R)$ is a constant (if the reaction is isokinetic), then from eqn. (7) a plot of ln $g(\alpha)$ versus $1/T$ will also be linear if the "correct" $g(\alpha)$ is used. Hence, the first step in this form of analysis is to test each $g(\alpha)$ to obtain the best fit to a straight line for ln $g(\alpha)$ versus $1/T$. The activation energy can then be calculated by differentiating ln $p(x)$ as follows

$$\frac{\mathrm{d}\ln p(x)}{\mathrm{d}x} = \left(\frac{1}{p(x)}\right)\left(\frac{\mathrm{d}p(x)}{\mathrm{d}x}\right) \tag{9}$$

which, by definition, is

$$= \left(\frac{1}{p(x)}\right)\left(\frac{-\mathrm{e}^{-x}}{x^2}\right) \tag{10}$$

or

$$= \frac{-1}{x^2\,\mathrm{e}^x p(x)} \tag{11}$$

Since $x = E/RT$ this becomes

$$\frac{\mathrm{d}\ln p(x)}{\mathrm{d}(1/T)} = \frac{-E}{Rx^2\,\mathrm{e}^x p(x)} \tag{12}$$

Thus the second step, having obtained two parallel lines [ln $p(x)$ and ln g

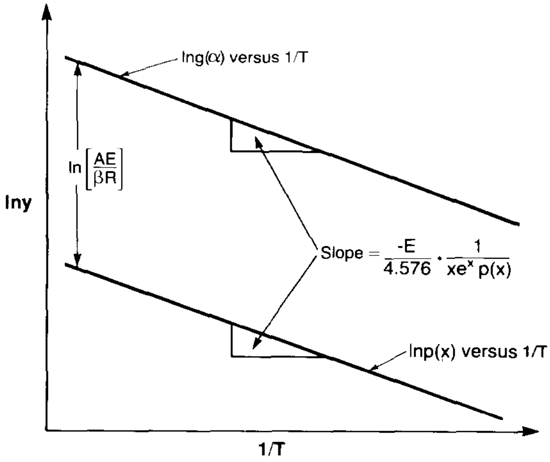

Fig. 1. Kinetic plot for the calculation of A and E.

(α) versus $1/T$] is to determine the slope (Fig. 1). In practice it is the ln $g(\alpha)$ versus $1/T$ plot that must be used since $p(x)$ cannot be accurately defined initially. Thus the slope is substituted into eqn. (12) to calculate E. At first a "guess" is made for E in the equation $x = E/RT$ and then a series of iterative loops are performed, so enabling E to be calculated to a greater accuracy.

Having calculated E the third step is to find the value of A. This is calculated from the distance between the two lines, as shown in Fig. 1. An algorithm describing the entire process has been described by Skvara and Sestak [10] and this was used as a basis for the program developed here.

DESCRIPTION OF THE PROGRAM

The program algorithm is shown in Table 1. This is similar to that described by Skvara and Sestak [10] except that they considered three α–T regions; the initial ($\alpha = 0.03$–0.35) the intermediate ($\alpha = 0.3$–0.8), and the

TABLE 1

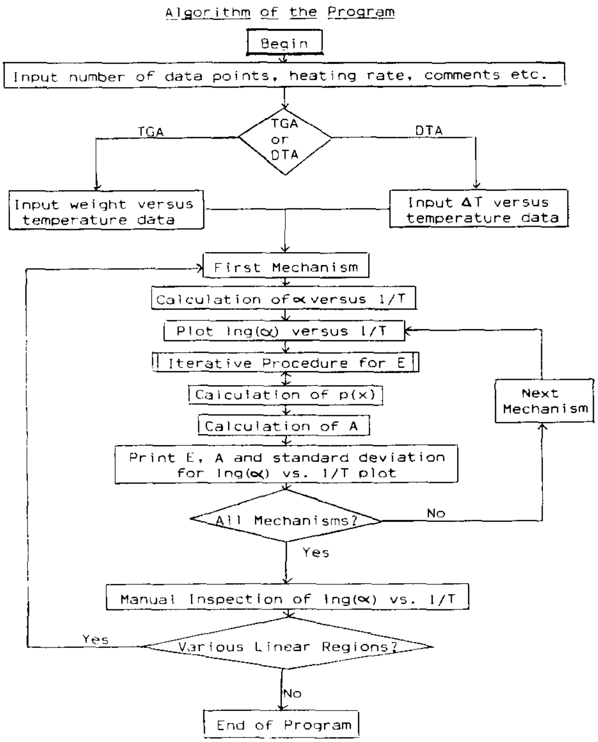

TABLE 2

Kinetic models used in the program

Model No.	Integral function of α $g(\alpha) =$
1	$2[1-(1-\alpha)^{1/2}]$
2	$3[1-(1-\alpha)^{1/3}]$
3	$3/2[1-(1-\alpha)^{2/3}]$
4	$-\ln(1-\alpha)$
5	$(1-\alpha)\ln(1-\alpha)+\alpha$
6	$[(1+\alpha)^{1/2}-1]^2$
7	$3/2[1-2/3\alpha-(1-\alpha)^{2/3}]$
8	$3/2[1/(1-\alpha)^{1/3}-1]^2$
9	$2\alpha^{1/2}$
10	$\exp[-(1-\alpha)]-\exp(-1)$

final ($\alpha = 0.7$–0.97). The linearity of each $\ln g(\alpha)$ versus $1/T$ plot was examined over each region and so it was possible to obtain three different mechanisms, each describing a different stage of the reaction. In our experience it is preferable to inspect manually each $\ln g(\alpha)$ versus $1/T$ plot across the entire experimental range and to then repeat the kinetic analysis over any regions of linearity which are apparent. The best fit was given by the lowest standard deviation as measured in the x direction [11].

For the calculation of E an initial guess must be made to begin the iterative loop. This is taken as the slope of the plot divided by the mid-temperature of the region of interest. The iterative loop is continued until two successive determinations agree to within 0.3 kJ mol^{-1}.

The mechanisms examined by this program include those shown in Table 2. A drawback of this form of integral method is that certain types of function become analytically indistinguishable. An example is the Avrami [12] type of equation, shown here as

$$(-\ln(1-\alpha))^n = kt \tag{13}$$

This is plotted as $n\ln[-\ln(1-\alpha)]$ versus $1/T$ and so different values of n simply shift the line and the resultant data must be treated with caution. If functions of this type are found to give the best fit, then the values of E and A must be examined. Some values of n will give completely unrealistic E and A values and so least a range of values of n can be settled on. Other functions which give rise to this problem include

$$\alpha^n = kt \tag{14}$$

and

$$\left(1-(1-\alpha)^{1/2}\right)^n = kt \tag{15}$$

Theoretical data

Theoretical data [13] obtained by assuming $E = 125$ kJ mol^{-1}, $\ln A = 15.4$ (A; min^{-1}) and a heating rate of 1 K min^{-1}, was used to test the program. The data was calculated using eqn. (6) to solve for α at temperature intervals of 2 K starting at around 400 K. Table 3 shows the result of analyzing the data using the program developed here. In each case the appropriate function gave a plot of lowest standard deviation (s.d.). The second ranked function data is also shown and, in most cases, the standard deviation is around an order of magnitude higher. This confirms that the program operates as intended.

Brown and Galwey [14], in a study of the distinguishability of kinetic models in isothermal kinetic analysis, discussed the source and magnitude of experimental errors. They conclude that in any thermal analysis study, the determination of α will give rise to errors of the most significance. By adding a random error to theoretical data they show that the distinguishability between kinetic models can be impaired. At error levels of > 5% the incorrect model may be selected using their method. For this study we have randomly incorporated up to ±2.5%, ±5% and ±10% errors into the α values for the ten test functions and tabulated the first and second ranked functions (Tables 4–6). The data obtained show that at a ±2.5% error level the standard deviations for the first and second ranked functions are extremely close and in one case (function 10) are coincident. At ±5% and ±10% error levels an incorrect function is frequently ranked first. This demonstrates that experimental data must be accurate to better than 97.5% in order to obtain meaningful kinetic parameters using this rising tempera-

TABLE 3

Test of a kinetic program using theoretical data

Test function [a]				Second ranked function			
Model No.	E (kJ mol^{-1})	$\ln A$	s.d. ($\times 10^{-6}$)	Model No.	E (kJ mol^{-1})	$\ln A$	s.d. ($\times 10^{-6}$)
1	125.7	15.9	0.0669	5	35.3	244.8	0.849
2	125.7	16.1	0.0662	2	14.6	125.2	2.89
3	125.7	15.8	0.0463	5	36.8	263.6	0.254
4	125.7	16.4	0.0897	1	12.4	230.6	9.52
5	125.6	15.3	0.117	5	4.8	122.1	0.871
6	125.7	14.2	0.0885	9	0.1	26.2	1.85
7	125.6	14.8	0.104	7	5.4	126.2	1.69
8	125.9	15.1	0.581	1	3.1	102.8	22.9
9	125.7	16.5	0.00747	5	74.8	581.0	0.429
10	125.7	15.2	0.0418	1	34.6	254.5	0.715

[a] From Table 2.

TABLE 4

Test of a kinetic program using theoretical data with a 2.5% random error

Test function No.	First ranked function			Second ranked function		
	No.	*E* (kJ mol^{-1})	s.d. ($\times 10^{-6}$)	No.	*E* (kJ mol^{-1})	s.d. ($\times 10^{-6}$)
1	1	124.9	1.11	7	256.8	1.26
2	2	124.5	1.82	1	116.7	3.36
3	3	124.9	1.01	5	260.4	1.02
4	4	123.6	3.58	8	304.1	7.79
5	5	124.9	1.96	3	57.6	2.42
6	6	124.8	1.52	9	26.0	2.75
7	7	124.5	2.30	3	54.3	2.70
8	8	125.3	21.8	4	48.5	22.7
9	9	124.9	0.39	6	505.6	0.42
10	10	125.0	1.02	3	161.1	1.02

TABLE 5

Test of a kinetic program using theoretical data with a ±5.0% random error

Test function No.	First ranked function			Second ranked function		
	No.	*E* (kJ mol^{-1})	s.d. ($\times 10^{-6}$)	No.	*E* (kJ mol^{-1})	s.d. ($\times 10^{-6}$)
1	7	255.5	2.16	1	124.2	2.21
2	2	123.7	3.43	1	116.0	4.15
3	5	259.0	1.98	3	124.0	2.02
4	4	122.5	6.54	2	104.5	8.96
5	5	124.3	3.90	3	57.3	4.42
6	6	124.0	3.03	9	25.7	4.04
7	3	53.8	4.49	7	123.4	4.53
8	8	120.9	14.1	4	47.1	21.8
9	6	502.3	0.69	9	124.0	0.79
10	3	115.4	1.81	5	241.4	1.83

TABLE 6

Test of a kinetic program using theoretical data with a ±10% random error

Test function No.	First ranked function			Second ranked function		
	No.	*E* (kJ mol^{-1})	s.d. ($\times 10^{-6}$)	No.	*E* (kJ mol^{-1})	s.d. ($\times 10^{-6}$)
1	3	117.3	4.16	5	244.8	4.22
2	1	249.8	5.96	2	125.2	5.98
3	3	126.5	3.22	5	263.6	3.22
4	2	116.1	6.41	1	230.6	6.43
5	9	20.2	7.20	5	122.1	7.57
6	6	126.0	5.84	9	26.2	5.94
7	10	61.2	9.54	7	126.2	9.70
8	2	49.1	15.8	1	102.8	18.1
9	3	285.1	1.82	5	581.0	1.82
10	2	126.4	4.15	1	254.5	4.21

ture kinetic method. This may also apply to other methods, many of which use a more approximate form of $p(x)$ than that used here and so already incorporate a larger degree of error.

Experimental data

Polystyrene

The TGA and DSC data, obtained by heating polystyrene in argon, was analyzed across the entire decomposition process. The $\ln g(\alpha)$ versus $1/T$ plots indicated an isokinetic process and Avrami type expressions [eqn. (13)] to have the best fit with the standard deviations of 3.74×10^{-7} and 6.20×10^{-7}. Comparison of these values with those obtained using theoretical data (Tables 3–6) suggests that the experimental error is $< \pm 2.5\%$ and so the kinetic parameters can be used with confidence. Assuming $n = 1$, then the obtained data is shown in Table 7 together with literature data for this process. Polystyrene has been studied by several investigators [15] and shown to have an activation energy of between 155 and 254 kJ mol^{-1} with a first-order mechanism [i.e. $n = 1$ in eqn (13)]. For $n = 1$ the program tested here gave a value of $E = 264$ kJ mol^{-1} for TGA and $E = 308$ kJ mol^{-1} for DSC. However, as Khanna and Pearce [16] noted, the exact value will depend on the precision of computation, the range used and the experimental variables. They obtained a value of $E = 224$ kJ mol^{-1}, for a first-order mechanism.

Polyamide

The second set of experimental data used was for the TGA of a polyamide (poly-1,3-phenyleneisophthalamide), shown in Fig. 2 [15]. The data were normalized over the first step, i.e. ~ 300–510 °C, assuming that this would be a total of 20% weight loss. Analysis of this step showed that functions of the type shown by eqn. 13 had the lowest standard deviation (6.02×10^{-6}). However, as can be seen by the plot of $\ln g(\alpha)$ versus $1/T$ for a first-order expression (Fig. 3), it is clear that there are two linear regions. Re-analyzing the data over these two regions results in a lower standard deviation for both the first region (3.43×10^{-6}) and the second region (5.75×10^{-7}), with an order type expression remaining as the best fit. The standard deviations for the $\ln g(\alpha)$ versus $1/T$ plot (Fig. 3), when compared to those obtained for the theoretical data (Tables 3–6), suggest that the experimental data can be used with confidence. The first region corresponds to a decomposition range of 0–12% when considering the total shown in Fig. 2. The activation energy was calculated as 214 kJ mol^{-1} for the first-order expression (Table 7). Literature data [16] for the same material reports a value of 215 ± 8 kJ mol^{-1}, over the range 0–15%. This was found using the method of Ozawa [17], which does not require a knowledge of the mechanism. The second region, observed using the procedure described here, gave

TABLE 7

Test of kinetic program using experimental data

Material	Technique	Data obtained using program				Literature data [14]		
		Range α	Model	E (kJ mol^{-1})	s.d. ln $g(\alpha)$ vs. $1/T$	Range α	Model	E (kJ mol^{-1})
Polystyrene (Polystyrol)	TGA	0.01–0.91	First order	264	6.20×10^{-7}	Various	First order	164–252
	DSC	0.03–0.99	First order	308	3.74×10^{-7}	0.25–0.85	First order	224
Poly(1,3-phenyleneisophthalamide) (Nomex)	TGA	0–0.12	First order	214	1.3×10^{-6}	0–15	First order	215 ± 8
		0.12–0.20	First order	162	5.75×10^{-7}	Not detected		
	DSC	0–0.07	Second order	261	1.15×10^{-6}	Not detected		
		0.08–0.30	Second order	121	1.93×10^{-6}	Not detected		

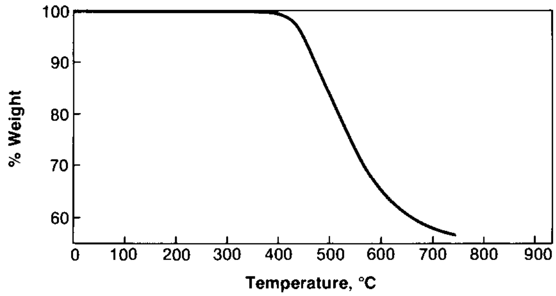

Fig. 2. TGA for the degradation of a polyamide.

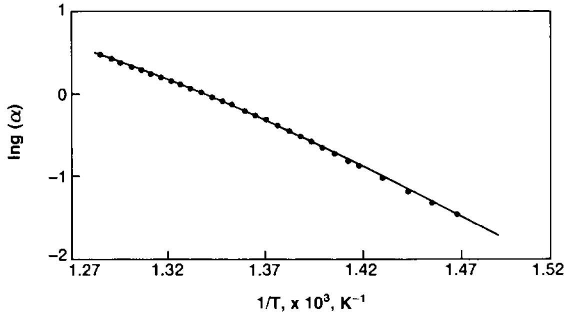

Fig. 3. Plot of ln $g(\alpha)$ versus $1/T$ for a polyamide.

an activation energy of 162 kJ mol^{-1}. This region had not been previously detected and this suggests that this method of kinetic analysis may be more versatile and sensitive than many others.

DSC data for the degradation of the polyamide under identical conditions to the TGA experiment, was analyzed in a similar manner. However, the standard deviation values obtained are somewhat large, suggesting that caution should be used in interpreting the results. Indeed, the model selected is a second-order type, which does not agree with either the TGA results or the previously published data (Table 7). This confirms that attention should be paid to the standard deviation values, as with the large errors an incorrect mechanism may be selected.

CONCLUSIONS

The development of a kinetic analysis method must include a study of the effects of possible errors in the experimental data before results can be used with any confidence. The results of such a study described here suggest that experimental errors of $\geqslant \pm 2.5\%$ may lead to incorrect kinetic parameters being obtained.

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