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KINETIC ANALYSIS USING TWO NON-ISOTHERMAL EXPERIMENTS. COMPARISON AMONG INTEGRAL SIMPLE METHODS TO DETERMINE KINETIC REACTION PARAMETERS

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ABSTRACT

The kinetic parameters E and Z (apparent activation energy and global frequency factor) and the model function $g(\alpha)$ that best fits simulated experiments in non-isothermal analysis are determined by three integral simple methods. It is proved that one of these methods (method B) has the greatest potential to choose the model function $g(\alpha)$ that best fits the non-isothermal experiments. A statistic comparison is made among these methods in the calculation of E and log Z.

INTRODUCTION

Quantitative mathematical description in thermal analysis is directed to the determination of kinetics because in that way the reactions and processes involved can be better understood [1].

Šesták [2] and Kríz and Šesták [3] highlighted methodological problems in the study of kinetic reactions by thermal analysis and warned about the manipulation of data, and inappropriate mathematical procedures, thus assuming that greater efforts to improve them were not essential. Although those recommendations are justified, we believe there are several reasons not to end discussion on the method of analysis of experimental data in thermal analysis. Maciejewski [4] put forward some interesting comments, and we think it necessary to add some others.

To begin with, studies on heterogeneous non-isothermal kinetics (e.g. refs. 5-21) have stressed: (a) the determination of model function, $f(\alpha)$ or $g(\alpha)$, that best describes the reaction mechanism, or (b) the evaluation of kinetic parameters E and Z (apparent activation energy and global frequency factor), either assuming previous knowledge of the reaction mechanism or

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independently of it. Nevertheless, there are few works which stress the joint importance of $g(\alpha)$ (or $f(\alpha)$), E and Z, which would allow reasonable conclusions to be reached on thermal decomposition kinetics [22–25].

On the other hand, in most cases, the scope or potential value of the methods for discrimination of probable and/or not probable $g(\alpha)$ has not been clarified; this has also been the case for the accuracy and precision with which E and Z have been determined.

Therefore the aim of this work is to determine the E and Z parameters and the integral model function $g(\alpha)$ that best fit simulated data from thermoanalytical techniques (e.g. differential scanning calorimetry (DSC), thermogravimetry (TG)) by three methods based on different approximations of the Arrhenius integral. These methods are compared by analysing their potential to differentiate mechanisms, their sensitivity to variation of the parameters involved in the suggested expressions, and the accuracy and precision with which kinetic parameters E and Z are obtained.

THEORY

Integration of the expression of rate of irreversible decomposition of solids, assuming that the pressure of gaseous products remains constant, results in

$$g(\alpha)=\int_0^{\alpha} f^{-1}(\alpha)\,\mathrm{d}\alpha=\frac{Z}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{1}$$

The problem in eqn. (1) lies in the resolution of the integral of the last term (the Arrhenius integral). The first approximation generally accepted is to assume

$$I=\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T\cong\int_0^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{2}$$

From eqn. (2) we work with three different approximations of this integral, which give the following suggested methods.

Method A

This is based on the Doyle approximation [26]. Thus eqn. (1) is expressed as follows:

$$I=\frac{E}{R}p(x) \tag{3}$$

where $x=E/RT$, and $\ln p(x)=-5.3305-1.0527x$ $(20<x<60)$. Then, considering eqns. (1) and (3), for two experiments carried out at two different heating rates β, and $T_{j,i}$ being the temperature for conversion $\alpha_{j,i}$ at a heating rate β_j, we obtain

$$\ln\left[\frac{g(\alpha_{j,i})\beta_j}{g(\alpha_{j+n,i+m})\beta_{j+n}}\right] = -1.0527\frac{E}{R}\left(\frac{1}{T_{j,i}} - \frac{1}{T_{j+n,i+m}}\right) \tag{4}$$

Method B

Approximation of integral I (eqn. (2)), has been expressed by Gorbachev [27] as follows:

$$I = \frac{RT^2}{E} \exp(x)\ p_k(x) \tag{5}$$

where different expressions for $p_k(x)$ have been used by various authors:
(1) Coats–Redfern

$$p_1(x) = 1 - \frac{2}{x} + \frac{6}{x^2} + \ldots$$

(2) Gorbachev–Schömilch

$$p_2(x) = \left(1 + \frac{2}{x}\right)^{-1}$$

(3) Balarin

$$p_3(x) = \left(1 + \frac{4}{x}\right)^{-1/2}$$

(4) Zsakó

$$p_4(x) = \frac{x^2}{(x-d)(x+2)}, \qquad d = \frac{16}{x^2 - 4x + 8}$$

For $x > 10$ different approximations $p_k(x)$ give similar values. Besides, in this case, it is true that

$$\frac{p_k(E/RT_{j,i})}{p_k(E/RT_{j+n,i+m})} \simeq 1 \tag{6}$$

if $x_{j,i}$, $x_{j+n,i+m}$ values are close.

Considering eqns. (1) and (5) and applying eqn. (6) we obtain

$$\ln\left[\frac{g(\alpha_{j,i})\beta_j T_{j+n,i+m}^2}{g(\alpha_{j+n,i+m})\beta_{j+n} T_{j,i}^2}\right] = -\frac{E}{R}\left(\frac{1}{T_{j,i}} - \frac{1}{T_{j+n,i+m}}\right) \tag{7}$$

This is a generalized expression of that used by Reich and Stivala [21] in their iterative method for the particular case in which $g(\alpha) = 1 - (1 - \alpha)^n$.

Method C

The approximation of integral I according to Senum and Yang [28] is

$$I = T\exp(-x)\left(\frac{x^2+10x+18}{x^3+12x^2+36x+24}\right) \tag{8}$$

For very close temperature values ($T_{j,i}$, $T_{j+n,i+m}$), with a relative difference below or equal to 5%, the expression between brackets in eqn. (8) does not differ greatly.

From that stated above and eqn. (8), for two experiments carried out at different heating rates, the following expression is obtained:

$$\ln\left[\frac{g(\alpha_{j,i})\beta_j T_{j+n,i+m}}{g(\alpha_{j+n,i+m})\beta_{j+n} T_{j,i}}\right] = -\frac{E}{R}\left(\frac{1}{T_{j,i}} - \frac{1}{T_{j+n,i+m}}\right) \tag{9}$$

Now, from eqns. (4), (7) and (9), we see that the graph for the first term vs. the expression between brackets in the last term is a straight line, the intercept of which on the ordinate has to be equal to zero. E is obtained from the slope value. On the other hand, from the approximations of integral I (eqns. (3), (5) and (8)), and from eqn. (1), Z is obtained.

In method A, and because of the error in the Doyle approximation, the E values obtained from eqn. (4) are improved by applying the correction suggested by Flynn [29].

EVALUATION PROCEDURE

To test the suggestion above and verify considerations stated earlier, 26 different model functions $g(\alpha)$ were used (as listed in Table 1) to simulate experimental α–T curves with the test values shown in Table 2 for α

TABLE 1

Integral model functions $g(\alpha)$ corresponding to solid decomposition reactions chosen from the literature

Code number	$g(\alpha)$	
1, 2	$[1-(1-\alpha)^{1/3}]^n$	$n = 2, \frac{1}{2}$
3	$[1-(1-\alpha)^{1/2}]^{1/2}$	
4	$[(1+\alpha)^{1/3}-1]^2$	
5	$[(1-\alpha)^{-1/3}-1]^2$	
6–12	$[-\ln(1-\alpha)]^n$	$n = 1, \frac{2}{3}, \frac{1}{2}, \frac{1}{3}, 4, 2, 3$
13–18	$1-(1-\alpha)^n$	$n = \frac{1}{2}, 3, 2, 4, \frac{1}{3}, \frac{1}{4}$
19–24	α^n	$n = 1, 2, \frac{3}{2}, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}$
25–26	$\frac{1}{n}[(1-\alpha)^{-n}-1]$	$n = 1, 2$

TABLE 2

Model function $g(\alpha)$ and values of parameters E, log Z and β used to simulate experimental $\alpha-T$ curves

$g(\alpha)$	Parameter values			
	E (kJ mol^{-1})	log Z (Z in s^{-1})	β_j (K min^{-1})	β_{j+n} (K min^{-1})
1–26	120	13.0	2	4
1, 6, 9, 18, 23	120	13.0	8	16
	80	13.0	2	4
	270	13.0	2	4
	120	8.0	2	4
	120	18.0	2	4

between 0.01 and 0.99. The Arrhenius integral values were obtained from the Senum and Yang expression [28], as this provides values with error below 10^{-2}%. The E, Z and β values shown in Table 2 were selected taking into account the range of experimental values of solid decomposition reactions most commonly found in the literature. Model functions $g(\alpha)$ 1, 6, 9, 18 and 23 were chosen, taking into account the five types of mechanisms suggested by Šesták and Berggren [30].

The values for the intercept on the ordinate, E and the correlation coefficient for the 26 model functions were calculated using eqns. (4), (7) and (9) for each method. Log Z was then calculated from eqn. (1) by applying the approximation of integral I used in each method. To calculate log Z for method B the Coats–Redfern three-term expression was selected.

RESULTS

Here follow the results of the calculations performed on the basis of the potential of the methods to differentiate mechanisms, their sensitivity to variation of the parameters involved (E, Z, $g(\alpha)$ and β), and their accuracy and precision in calculating E and Z.

Potential of the methods to differentiate model function $g(\alpha)$

From theory, on applying eqns. (4), (7) and (9) to (simulated) experimental data, the $g(\alpha)$ that best represents the decomposition mechanism will result in a straight line with intercept value closest to zero. The results of our calculations show that although many model functions $g(\alpha)$ give highly significant correlation coefficients, only one of them (that of the simulation of the experimental curve) yields an intercept value remarkably closer to zero than the rest. As they are simulated curves without experimental error

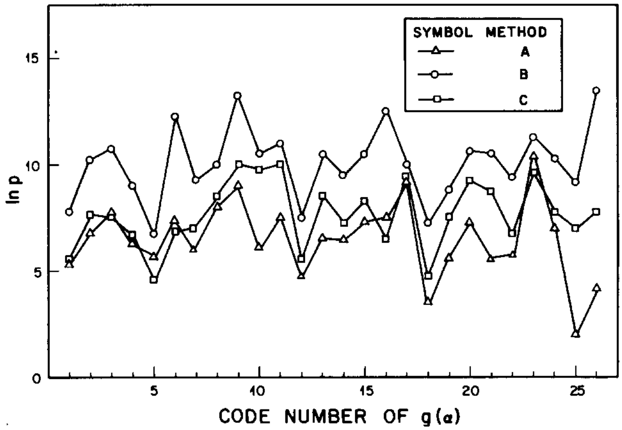

Fig. 1. Potential of methods A, B and C to differentiate the true model function. Values used to simulate the α–T curves: $E = 120$ kJ mol^{-1}, log $Z = 13.0$ (Z in s^{-1}), $\beta_j = 2$ K min^{-1} and $\beta_{j+n} = 4$ K min^{-1}.

the correlation coefficient values for $g(\alpha)$ closest to zero equal 1.000. Thus the value of the intercept can be used to choose the mechanism for the solid decomposition reaction that best fits the experimental data from the thermoanalytical techniques mentioned above.

Nevertheless, although there are other values of intercept on the ordinate also close to zero, for the sake of comparison we define the potential **p** of the true model function (with which the experimental data were simulated) as follows:

$$\mathbf{p} = \ln\left(\frac{|a_{\mathrm{T}} - a_{\mathrm{i}}|}{a_{\mathrm{T}}}\right) \tag{10}$$

where a_{T} and a_{i} are the values of the intercept on the ordinate closest to zero (from a total of 26 model functions), a_{T} corresponding to the true model function.

Figure 1 shows the results of **p** for each method and each model function, for the following values: $E = 120$ kJ mol^{-1}, log $Z = 13.0$ (Z in s^{-1}), $\beta_j = 2$ K min^{-1} and $\beta_{j+n} = 4$ K min^{-1} with which the α–T curves were simulated. It can be clearly seen that, in all cases, method B has a greater potential to differentiate the true model function. Methods C and A follow, in that order, although there is alternation in some cases. This characteristic was confirmed when E, Z and β values are varied, taking as pivots model functions 1, 6, 9, 18 and 23.

Sensitivity to variation of the parameters involved

The sensitivity to variation of the parameters involved has been studied in the calculation of E and log Z by the analysis of variance (Tables 3 and 4).

TABLE 3

F values for the analysis of variance in calculating E according to the method applied

Method	F values[a]			
	E[b] = 120, log Z[c] = 13.0		E[b] = 120, β_j[d] = 2, β_{j+n}[d] = 4	
	$g(\alpha)$	β_j, β_{j+n}	$g(\alpha)$	log Z
A	1.40	0.19	0.57	1.74
B	104.87[e]	8.03[e]	4.07[f]	223.85[e]
C	4808.80[e]	261.57[e]	8.87[e]	469.79[e]

[a] d.f. $[g(\alpha)] = 4$, d.f. (log Z) = 2, d.f. $(\beta) = 5$.
[b] In kJ mol^{-1}.
[c] In s^{-1}.
[d] In K min^{-1}.
[e] $P < 0.01$.
[f] $P < 0.05$.

The homogeneity was previously proved by the Cochran method [31]. It is concluded from Table 3 that in the calculation of E the only method that does not show any significant difference is method A, whereas the others do, in every case. From Table 4 it is concluded that in the calculation of log Z the only method that shows significant differences is method B, except for E variations. Therefore, method A proves to be the only one that is statistically non-sensitive to parameter variations in the calculation of both E and log Z, method B being the most sensitive to variation in both cases. Method C is sensitive to variation in parameters only in the calculation of E.

Accuracy and precision in the calculation of E and log Z parameters

The analysis of accuracy and precision was carried out for the following values: $E = 120$ kJ mol^{-1}, log $Z = 13.0$ (Z in s^{-1}), $\beta_j = 2$ K min^{-1} and $\beta_{j+n} = 4$ K min^{-1} with which α–T curves were simulated.

TABLE 4

F values for the analysis of variance in calculating log Z according to the method applied

Method	F values[a]			
	E[b] = 120, log Z[c] = 13.0		log Z[c] = 13.0, β_j[d] = 2, β_{j+n}[d] = 4	
	$g(\alpha)$	β_j, β_{j+n}	$g(\alpha)$	E
A	1.13	0.67	2.30	0.26
B	41.94[e]	4.22[e]	58.33[e]	3.48
C	2.67	2.64	1.07	3.24

[a] d.f. $[g(\alpha)] = 4$, d.f. $(E) = 5$, d.f. $(\beta) = 5$.
[b] In kJ mol^{-1}.
[c] In s^{-1}.
[d] In K min^{-1}.
[e] $P < 0.01$.

TABLE 5

Accuracy and precision in calculating E according to the different methods; values used in the simulation: $E = 120$ kJ mol^{-1}, $\log Z = 13.0$ (Z in s^{-1}), $\beta_j = 2$ K min^{-1} and $\beta_{j+n} = 4$ K min^{-1}

Method	$\langle E \rangle$ (kJ mol^{-1})	$\sigma^{\mathrm{a}}_{\langle E \rangle}$ (kJ mol^{-1})	V.C. [b] (%)	Relative error (%)
A	119.93	0.10849	0.09	0.06
B	119.84	0.01397	0.01	0.13
C	123.23	0.71950	0.58	2.69

[a] Standard deviation.
[b] Variation coefficient.

TABLE 6

Accuracy and precision in calculating log Z according to the different methods; values used in the simulation: $E = 120$ kJ mol^{-1}, $\log Z = 13.0$ (Z in s^{-1}), $\beta_j = 2$ K min^{-1} and $\beta_{j+n} = 4$ K min^{-1}

Method	$\langle \log Z \rangle$ (Z in s^{-1})	$\sigma_{\langle \log Z \rangle}$	V.C. (%)	Relative error (%)
A	12.866	0.01438	0.11	1.03
B	12.974	0.00127	0.01	0.20
C	13.422	0.00167	0.01	3.24

From the results in the calculation of E shown in Table 5, it is concluded that method A is the most accurate, whereas method B is the most precise. In the log Z calculation (Table 6) method B proves to be the most accurate and precise, whereas A is the least precise of the three.

CONCLUSIONS

The methods used in this study to calculate the kinetic parameters E and Z and the model function $g(\alpha)$ for decomposition of irreversible solids originated from a generalized expression such as

$$\ln\left[\frac{g(\alpha_{j,i})\beta_j T^u_{j+n,i+m}}{g(\alpha_{j+n,i+m})\beta_{j+n} T^u_{j,i}}\right] = -q\frac{E}{R}\left(\frac{1}{T_{j,i}} - \frac{1}{T_{j+n,i+m}}\right) \qquad (11)$$

where according to the method (A, C or B) $u = 0$, 1 or 2 and $q = 1.0527$, 1.0000 or 1.0000 respectively. The analysis of the potential of the methods presented, based on simulated α–T curves, proves to be highly specific in the choice of model function $g(\alpha)$ that gives the best fit to the simulated results, in the following order:

Method B > Method C > Method A

This methodology must be carefully applied to experimental data because of experimental error, basically in the curve ends [24,25], which can lead to wrong results in the choice of $g(\alpha)$.

Also, we consider that the only way to determine the process which the sample actually undergoes is to experiment with other techniques (isothermal decomposition, electronic microscopic, X-ray diffraction, etc.), the results of which complement the methodology discussed here.

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REFERENCES

1 G. Vårhegyi, Thermochim. Acta, 110 (1987) 95.
2 J. Šesták, J. Therm. Anal., 16 (1979) 503.
3 J. Kríz and J. Šesták, Thermochim. Acta, 110 (1987) 87.
4 M. Maciejewski, J. Therm. Anal., 33 (1988) 1269.
5 J.H. Flynn and L.A. Wall, Polym. Lett., 4 (1966) 323.
6 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881; J. Therm. Anal., 2 (1970) 301.
7 H.E. Kissinger, J. Res. Nat. Bur. Stand., 57 (1956) 217; Anal. Chem., 29 (1957) 1702.
8 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
9 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
10 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
11 A.J. Kassman, Thermochim. Acta, 84 (1985) 89.
12 J. Šesták, V. Šatava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
13 J. Šesták, Silikaty, 11 (1967) 153.
14 J.G. Murgulescu and E. Segal, Stnd. Cercet. Chim. Tom. (Bucharest), 15 (1967) 261.
15 C.D. Doyle, in P.E. Slude and L.T. Lenkis (Eds.), Techniques and Methods of Polymer Evaluation, Arnold, London, 1966, Vol. 1, Ch. 4.
16 V. Šatava and J. Škvåra, J. Am. Ceram. Soc., 52 (1969) 591.
17 L. Reich, J. Polym. Sci., Part A, 2 (1964) 1261.
18 J.M. Papazian, Met. Trans., Part A, 13 (1982) 761.
19 H. Tanaka and N. Koga, J. Therm. Anal., 32 (1987) 1521.
20 N. Koga and H. Tanaka, J. Therm. Anal., 34 (1988) 177.
21 L. Reich and S.S. Stivala, Thermochim. Acta, 55 (1982) 385.
22 A. Jerez, E. Ramos, M. Gaitån, M.L. Veiga and C. Pico, Thermochim. Acta, 115 (1987) 175.
23 C.G.R. Nair and P.M. Madhusudanan, Thermochim. Acta, 14 (1976) 373.
24 M. Maciejewski, Thermochim. Acta, 113 (1987) 287.
25 M. Maciejewski, J. Therm. Anal., 33 (1988) 243.
26 C.D. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.

27 V.M. Gorbachev, J. Therm. Anal., 25 (1982) 603.
28 G.I. Senum and R.T. Yang, J. Therm. Anal., 11 (1977) 445.
29 J.H. Flynn, J. Therm. Anal., 27 (1983) 95.
30 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
31 B.J. Winer, Statistical Principles in Experimental Design, McGraw-Hill, New York, 1971.