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The shape of thermoanalytical curves as a function of the reaction kinetics

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Abstract

The shape index S is a characteristic parameter of a thermoanalytical (TA) curve. It is demonstrated that S is a linear function of the ratio of the temperatures T_2/T_1 at two inflexion points of a TA curve. Both the intercept and slope of this function depend on the kinetic model. Therefore, it seems that all previously published papers neglecting the influence of the T_2/T_1 parameter are probably erroneous. The $S(T_2/T_1)$ relationship discussed in this paper permits certain conclusions about the most probable kinetic model to be made from a single TA curve.

INTRODUCTION

Thirty-five years ago, one of the most cited papers in TA kinetics was published [1]. In this paper, Kissinger presented simultaneously two different approaches to the kinetic analyses of TA data which affected the development of this field for many years. The first approach makes possible the determination of the activation energy regardless of the kinetic model, by recording multiple TA scans at different heating rates. The second approach was intended to determine the reaction order by analyzing the shape of a single TA curve, as shown in Fig. 1. While the first approach has been used successfully by many researchers to calculate activation energies, the second approach is rather problematic and there remain some doubts concerning its general applicability.

Several papers have since been published concerning the shape-index analysis of TA curves [2, 3] and of temperature-programmed desorption (TPD) curves [4–8]. Recently, we have analyzed the shape index of TPD data [9]. It was found that this concept can be very useful in elucidating the kinetic mechanism, particularly when no readsorption takes place. The aim of this paper is to discuss the applicability of this concept to the kinetic analysis of TA data.

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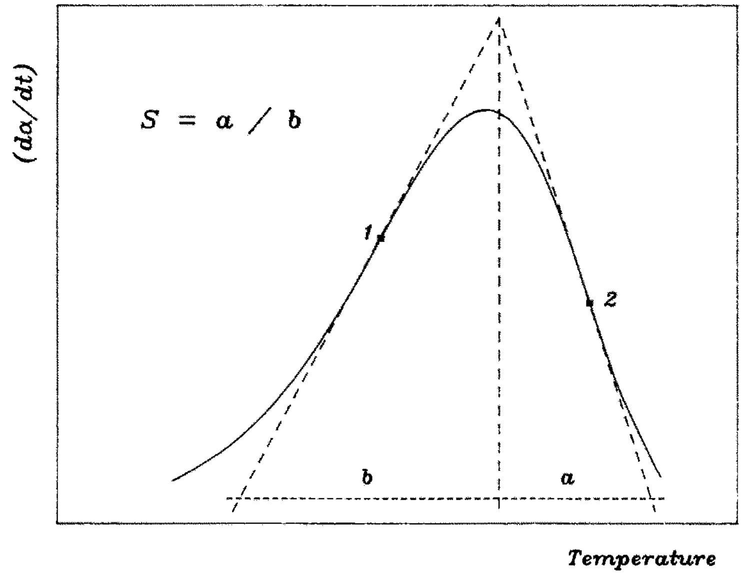

Fig. 1. Graphical method for the determination of the shape index S from a TA curve.

BASIC EQUATIONS AND KINETIC MODELS

The mathematical expression of the TA curve corresponding to the kinetic process is

$$d\alpha/dt = Ae^{-x}f(\alpha) \qquad (1)$$

where $d\alpha/dt$ is the reaction rate, A is the pre-exponential term and x is the reduced activation energy ($x = E/RT$). The function $f(\alpha)$ represents the mathematical expression of the kinetic model. The most frequently cited basic kinetic models are summarized in Table 1.

In addition to the basic kinetic models which correspond to certain geometries of the reaction interface, there are also empirical kinetic models

TABLE 1

The basic kinetic models [10]

Model	Symbol	$f(\alpha)$
Johnson–Mehl–Avrami	JMA(n)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
2-D reaction	R2	$(1-\alpha)^{1/2}$
3-D reaction	R3	$(1-\alpha)^{2/3}$
2-D diffusion	D2	$1/[-\ln(1-\alpha)]$
Jander eqn.	D3	$3/2(1-\alpha)^{2/3}/[1-(1-\alpha)^{2/3}]$
Ginstling–Brounshtein	D4	$3/2[(1-\alpha)^{-1/3}-1]$

TABLE 2

The empirical kinetic models [10]

Model	Symbol	$f(\alpha)$
Reaction order	RO(n)	$(1-\alpha)^n$
Šesták–Berggren	SB(m, n)	$\alpha^m(1-\alpha)^n$

(Table 2). The kinetic exponent n can be an integer or a fraction for both the RO(n) and SB(m, n) models. It is evident that the RO(n) model includes both the R2 and R3 models for $n = 1/2$ and $2/3$, respectively. Recently it was shown [11] that acceptable values of the parameter m for the SB(m, n) model are confined to the interval $0 < m < 1$.

The aim of the kinetic analysis of TA data is to find the most probable kinetic model which gives the best description of the studied process and allows the prediction of the reaction kinetics under defined conditions.

The shape index is defined according to Kissinger [1] as the absolute ratio of the slope of the tangents to the TA peak at the inflection points, which can be formulated analytically as

$$S = \frac{(\mathrm{d}^2\alpha/\mathrm{d}t^2)_{i=1}}{(\mathrm{d}^2\alpha/\mathrm{d}t^2)_{i=2}} \tag{2}$$

where subscripts $i = 1$ and $i = 2$ refer to the first and second inflection points, respectively.

Equation (1) can be integrated to give

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = -\frac{AE}{\beta R}\mathrm{e}^{-x}\left(\frac{\pi(x)}{x}\right) \tag{3}$$

where β is the heating rate applied in a TA experiment and the term $\pi(x)$ is an approximation of the temperature integral [10].

Differentiating eqn. (1) with respect to time, and combining with eqn. (3), we obtain the equation for the derivative of the TA peak in the form

$$(\mathrm{d}^2\alpha/\mathrm{d}t^2) = \left(\frac{\beta R x}{E\pi(x)}\right)^2 g(\alpha)f(\alpha)[f'(\alpha)g(\alpha) + x\pi(x)] \tag{4}$$

where $f'(\alpha) = \mathrm{d}f(\alpha)/\mathrm{d}\alpha$. From eqns. (2) and (4), a mathematical expression for the shape index of a TA peak is obtained

$$S = \left|\frac{f(\alpha_1)g(\alpha_1)[f'(\alpha_1)g(\alpha_1) + x_1\pi(x_1)]}{f(\alpha_2)g(\alpha_2)[f'(\alpha_2)g(\alpha_2) + x_2\pi(x_2)]}\right|\left[\frac{x_1\pi(x_2)}{x_2\pi(x_1)}\right]^2 \tag{5}$$

where α_1 and α_2 are the values of the degree of conversion at the first and

TABLE 3

Temperature integral approximations

Author	$\pi(x)$
Doyle [12]	$1/x$
Coats–Redfern [13]	$(1-2/x)/x$
Gorbatchev [14]	$1/(x+2)$
Balarin [15]	$(1-2/x+6/x^2+20/x^3)/x$
Senum–Yang [16] (2nd degree)	$(x+4)/(x^2+6x+6)$
Senum–Yang [16] (4th degree)	$(x^3+18x^2+88x+96)/(x^4+20x^3+120x^2+240x+120)$

second inflection points of a TA peak corresponding to the roots of the equation

$$\begin{aligned} &f'(\alpha_i)g(\alpha_i)[f'(\alpha_i)g(\alpha_i)+3x_i\pi(x_i)] \\ &\quad +f''(\alpha_i)f(\alpha_i)g^2(\alpha_i) \\ &\quad +x_i\pi(x_i)[x_i\pi(x_i)-2\pi(x_i)]=0 \end{aligned} \tag{6}$$

where $f''(\alpha)=\mathrm{d}^2f(\alpha)/\mathrm{d}\alpha^2$. From eqns. (5) and (6), it follows that the value of the shape index is affected by the term $\pi(x)$. There are many approximate expressions of $\pi(x)$ in the literature (see Table 3). According to our experience, the 4th-order rational expression of Senum and Yang [16] is relatively simple, and precise, and gives sufficiently accurate results.

THE SHAPE-INDEX ANALYSIS

It is important to note that both the shape index and the temperatures corresponding to the inflexion points can easily be determined from an experimental TA curve (or its differential form), as shown in Fig. 1. From a practical point of view, it is useful to plot the shape index as a function of the inflex temperature ratio (T_2/T_1) for a given kinetic model. This dependence corresponding to the first-order reaction RO(1) is shown in Fig. 2 for approximations of the temperature integral given in Table 3. It is obvious that the $S(T_2/T_1)$ dependences calculated from eqns. (5) and (6) using the Doyle [12], Coats–Redfern [13] and Balarin [15] approximations differ considerably from the more accurate $\pi(x)$ term calculated according to Senum and Yang [16].

Thus the equation for the shape index published by Kissinger [1] cannot

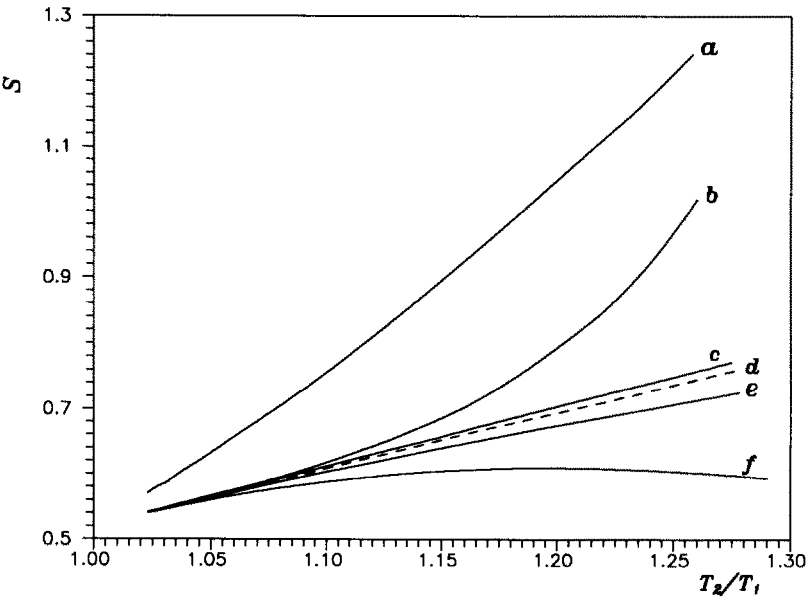

Fig. 2. The influence of the $\pi(x)$ term on the $S(T_2/T_1)$ dependence. The following approximations are used: a, Doyle [12]; b, Balarin [13]; c, Senum–Yang 4th-degree [16]; d, Senum–Yang 2nd-degree [16] (broken line); e, Gorbatchev [14]; f, Coats–Redfern [13].

give correct values of S; nor can that published later by Criado et al. [2] because of the Coats–Redfern [13] approximation used in their derivation. The equation for S derived by Ibok and Ollis [6] for TPD, assuming the Doyle approximation [12], is even more problematic. In later papers published by Criado et al. [7, 8], the temperature integral was well approximated by a more complicated series, but unfortunately the multiplicative factor $[x_2\pi(x_2)/x_1\pi(x_1)]$ is still missing from their equation for S. Therefore, all these previously published results are probably miscalculated.

It should be stressed that if a good approximation of the temperature integral is used, e.g. the 4th-degree Senum and Yang formula [16], then the solution of eqns. (5) and (6) leads to a linear relationship between S and T_2/T_1 for all the kinetic models summarized in Table 1, as shown in Fig. 3. From an inspection of Fig. 3, it can be seen that the $S(T_2/T_1)$ plots of the D3 and R3 models are identical. In addition, there is just one common curve corresponding to the JMA(n) model, regardless of the value of kinetic exponent n. The $S(T_2/T_1)$ functions cannot be calculated for the D2, D4 and RO($n \le 1/2$) models because the second inflexion point does not exist.

It was found that the linear relationship of the shape index versus the T_2/T_1 ratio can be described by the equation

$$S = S^{\infty} + K[(T_2/T_1) - 1] \tag{7}$$

The intercept S^{∞} in eqn. (7) corresponds to the shape index for the infinite

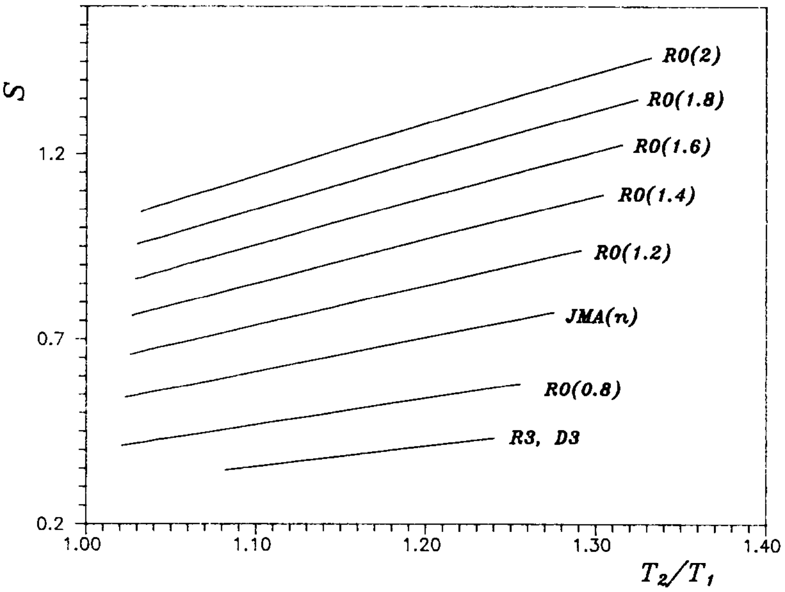

Fig. 3. The dependence of the shape index versus the ratio of temperatures at inflexion points plotted for the RO(n), D3 and JMA(n) models.

reduced activation energy x. In this case

$$\lim_{x \to \infty} [x\pi(x)] = 1 \tag{8}$$

and, therefore, eqn. (5) can be written in the form

$$S^\infty = \left| \frac{f(\alpha_1^\infty)g(\alpha_1^\infty)[f'(\alpha_1^\infty)g(\alpha_1^\infty)+1]}{f(\alpha_2^\infty)g(\alpha_2^\infty)[f'(\alpha_2^\infty)g(\alpha_2^\infty)+1]} \right| \tag{9}$$

The values of α_1^∞ and α_2^∞ corresponding to $x \to \infty$ are obtained from eqn. (5) rewritten in the form

$$f'(\alpha_i^\infty)g(\alpha_i^\infty)[f'(\alpha_i^\infty)g(\alpha_i^\infty)+3] + f''(\alpha_i^\infty)f(\alpha_i^\infty)g^2(\alpha_i^\infty) = -1 \tag{10}$$

These parameters are summarized in Table 4.

In Fig. 4, both the intercept and the slope corresponding to eqn. (7) are plotted for the RO(n) model as a function of the kinetic exponent. The filled squares show both the D3 and JMA(n) models which can be considered as special cases of the reaction order model RO(n). This is in a good agreement with previous results [17–20].

Kissinger [1] suggested a simple relationship between the shape index and the kinetic exponent for the RO(n) model of the form $S = 0.63n^2$. This relationship is shown in Fig. 5, plotted as the broken line. The solid lines in this figure were calculated using eqn. (7) for different values of the T_2/T_1 ratio. It is evident that the Kissinger relationship cannot be successfully

TABLE 4

The values of α at the inflexion of a DSC curve for $x \rightarrow \infty$

Model	α_1^∞	α_2^∞
JMA(n)	0.317	0.927
R2	0.438	–
R3	0.387	0.982
D2	0.528	–
D3	0.387	0.982
D4	0.464	–
RO(n)[a]	$1-\left[\dfrac{n-1 \pm (n^2+2n+4/n-7)^{1/2}}{4n-2}\right]^{1/n-1}$	

[a] This equation is valid for $n \neq 1/2$ and $n \neq 1$.

used for the estimation of the kinetic exponent because it does not take into account the effect of T_2/T_1. However, the $S(n)$ dependences plotted as solid lines in Fig. 5 are very useful for the estimation of the kinetic exponent for the RO(n) model, provided that both the shape index and T_2/T_1 have been determined from the TA curve.

Figure 6 shows the S versus T_2/T_1 dependences for the SB(m, n) model. It is clear that for a given value of the parameter n, the shape index increases with m. This figure also clearly demonstrates the flexibility of the SB(m, n) model: by combining both kinetic exponents m and n, we can obtain a

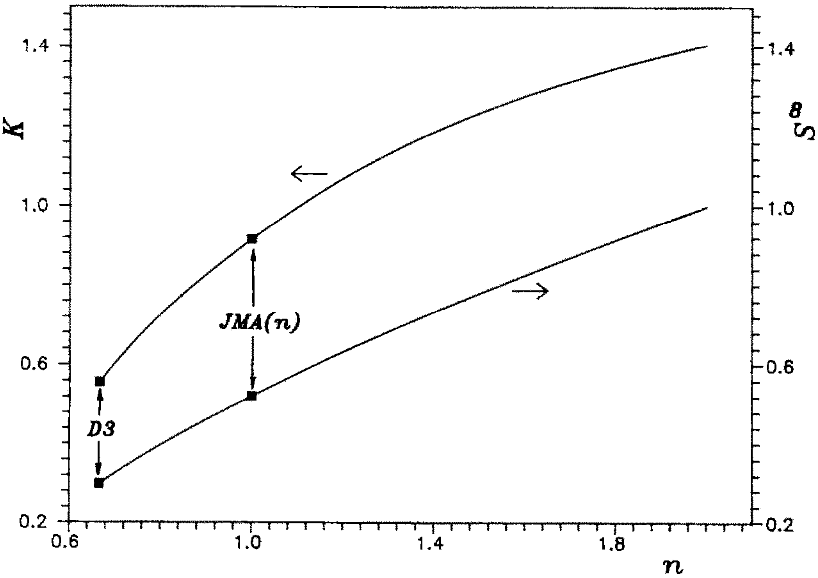

Fig. 4. The dependence of the parameters of eqn. (7) on the kinetic exponent for the RO(n) model. The solid squares correspond to the D3 and JMA(n) model, respectively.

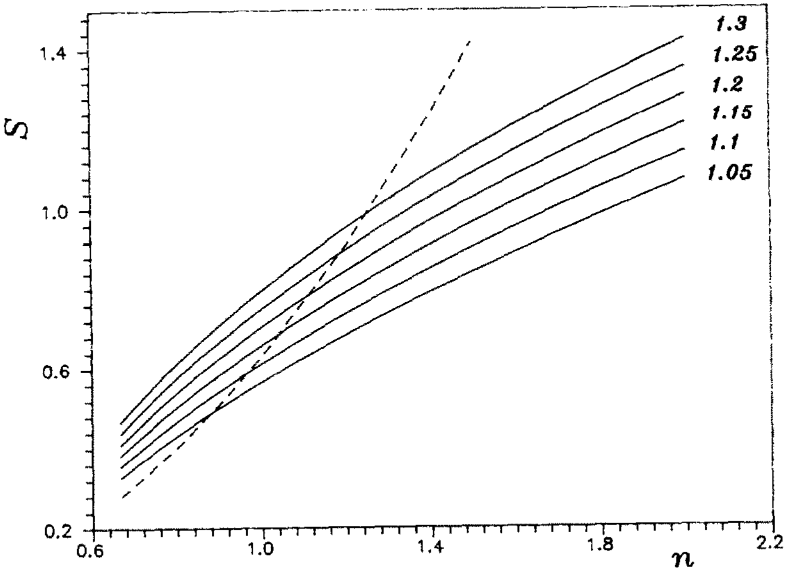

Fig. 5. The $S(n)$ plot for the RO(n) model (solid lines) calculated by eqn. (7) using data from Fig. 4. The numbers correspond to the values of T_2/T_1. The dependence proposed by Kissinger [1] (see text) is shown by the broken line.

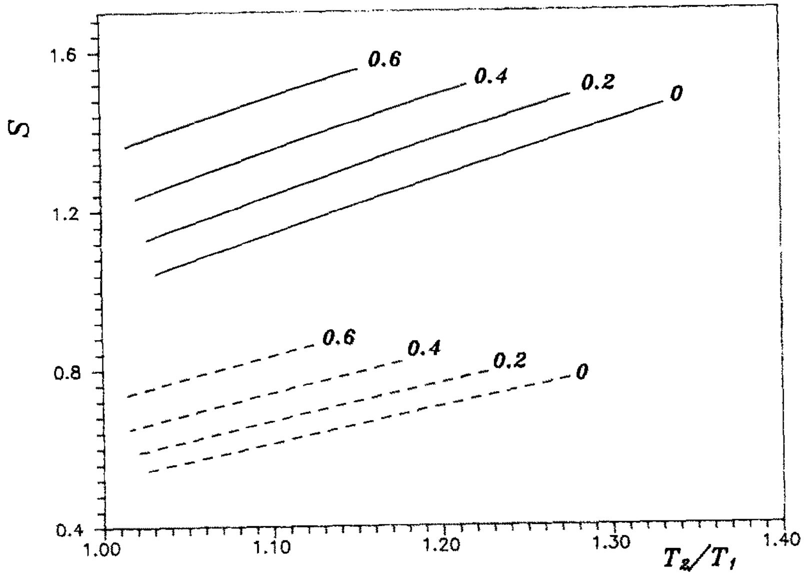

Fig. 6. The $S(T_2/T_1)$ dependence for the SB(m, n) model where $n = 1$ (broken lines) and $n = 2$ (solid lines). The numbers correspond to the value of the parameter m.

relatively broad range of S values for a given T_2/T_1 ratio. This range of the shape index evidently includes all the kinetic models discussed.

CONCLUSION

It has been demonstrated that the shape index is a linear function of the T_2/T_1 ratio for a sufficiently accurate approximation of the temperature integral term $\pi(x)$. From this point of view, shape analysis of a TA curve can give us a basic idea about the most probable kinetic model. Nevertheless, in order to verify the most suitable kinetic model, a complete kinetic analysis [21] of the experimental data should be performed.

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