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THE SHAPE OF A THERMOANALYTICAL CURVE AND ITS KINETIC INFORMATION CONTENT

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ABSTRACT

It is known that the mechanism of the kinetic process affects the shape of the corresponding thermoanalytical curve (TC). This paper presents a theoretical analysis of this problem. The inflexional asymmetry parameters are defined, expressing the asymmetry of the TC with respect to the degree of conversion and its first and second time-derivative. The possible application of these parameters in kinetic analysis is discussed.

INTRODUCTION

In the last twenty years thermoanalytical techniques, such as differential scanning calorimetry (DSC), differential thermal analysis (DTA) or thermogravimetry (TG), have become very popular and widely used for the characterisation and the study of various phase transformations and reactions.

Many papers have been published on the determination of the kinetic parameters from DSC, DTA, TG or other TCs [1–6]. These methods can be divided into two main groups: (i) multiple scan methods and (ii) single scan methods. It is well known [2] that multiple scan methods can be successfully used for the correct determination of the activation energy. However, it is still not clear whether it is possible, in principle, to obtain correct kinetic information by single scan methods. In our recent paper [6], we demonstrated a certain degree of scepticism in this respect concluding that without any additional information, e.g. the activation energy, the kinetic mechanism can hardly be ascertained using so-called master plots. It is the intent of this paper to continue the discussion of this question, analysing the shape of a TC and its implications for the kinetic analysis.

In the following section, we first briefly review the mathematical relationships used to describe a TC. A subsequent section presents a shape analysis

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of TC and the practical consequences for the extraction of kinetic information.

FUNDAMENTAL EQUATIONS

The mathematical expression for the differential thermoanalytical curve (DTC) corresponding to a kinetic process is usually written in the form

$$\dot{\alpha} = K(T)f(\alpha) \tag{1}$$

where $\dot{\alpha}$ is the time derivative of the degree of conversion, α. The first term on the right-hand-side of eqn. (1) is the Arrhenius rate constant, i.e. $K(T) = A \exp(-E/RT)$ and the second term, $f(\alpha)$, is an analytical expression describing the kinetic model of the process. The most frequently used $f(\alpha)$ functions [2] are summarised in Table 1. The parameters A and E, as well as the exponent n of $f(\alpha)$, are constants that represent the kinetic process.

For the sake of simplicity, it is convenient to introduce a new variable $x = E/RT$, called the reduced activation energy. The resulting equation for the DTC is then

$$\dot{\alpha} = A\, \mathrm{e}^{-x} f(\alpha) \tag{2}$$

If the temperature rises at a constant rate ($\beta = \dot{T}$), as is typical in thermal analysis, eqn. (2) cannot be integrated analytically and thus the approximate expression is obtained

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

There are several algorithms for the approximation of the term $\pi(x)$. In this paper we used the 4th-degree rational approximation of Senum and Yang [7]

TABLE 1

The kinetic models

Symbol	$f(\alpha)$
JMA(n)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
R0(n) [a]	$(1-\alpha)^n$
D2	$-1/\ln(1-\alpha)$
D3	$\dfrac{3(1-\alpha)^{2/3}}{2\left[1-(1-\alpha)^{1/3}\right]}$
D4	$\dfrac{3}{2\left[(1-\alpha)^{-1/3}-1\right]}$

[a] In the literature, the symbols R2 and R3 are used for $n = 1/2$ and $2/3$ respectively.

which calculates the $g(\alpha)$ function with an accuracy better than $10^{-5}\%$ for $x = 20$

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{4}$$

The T–α plot, i.e. the integral thermoanalytical curve (ITC), can be calculated by the solution of eqn. (3).

Differentiating eqn. (2) with respect to time and combining with eqn. (3), we obtain the equation for the derivative of the differential thermoanalytical curve (DDTC) in the form

$$\ddot{\alpha} = \left(\frac{\beta R}{E}\right)^2 \left[\frac{x}{\pi(x)}\right]^2 g(\alpha) f(\alpha) [f'(\alpha) g(\alpha) + x\pi(x)] \tag{5}$$

By setting eqn. (5) equal to zero, we get the equation that must be fulfilled by α_p and x_p at the maximum of the DTC

$$f'(\alpha_p) g(\alpha_p) + x_p \pi(x_p) = 0 \tag{6}$$

Similarly, using the condition $\ddot{\alpha} = 0$ we can obtain the equation for α_i and x_i corresponding to the inflexion points of the DTC

$$f'(\alpha_i) g(\alpha_i) [f'(\alpha_i) g(\alpha_i) + 3x_i \pi(x_i)] + f''(\alpha_i) f(\alpha) g^2(\alpha_i) + x_i \pi(x_i) [x_i \pi(x_i) - 2\pi(x_i)] = 0 \tag{7}$$

SHAPE ANALYSIS OF A TC

For a quantitative description of the shape of a TC it is useful to define certain quantities which are easily available from the experimental data. In this respect, we can define four parameters corresponding to a change of the variables x, α, $\dot{\alpha}$ and $\ddot{\alpha}$ between the maximum and the inflexion points of the DTC as illustrated in Fig. 1. The mathematical expression for these dimensionless inflexional asymmetry parameters are summarised in Table 2. The implication of the inflexional asymmetry for the extraction of kinetic information from the thermoanalytical data is discussed in detail below.

The inflexional asymmetry of x

The inflexional asymmetry of the DTC with respect to the reduced activation energy is expressed by the parameter Δx_i corresponding to the first ($i = 1$) and the second ($i = 2$) inflexional points of the DTC, respectively. Unfortunately, this parameter cannot be expressed explicitly. We calculated, therefore, the set of the DDTC using eqns. (3) and (5) (see Fig. 1c) and then determined x_p and x_i numerically. The parameter Δx_i was then calculated by the formula given in Table 2.

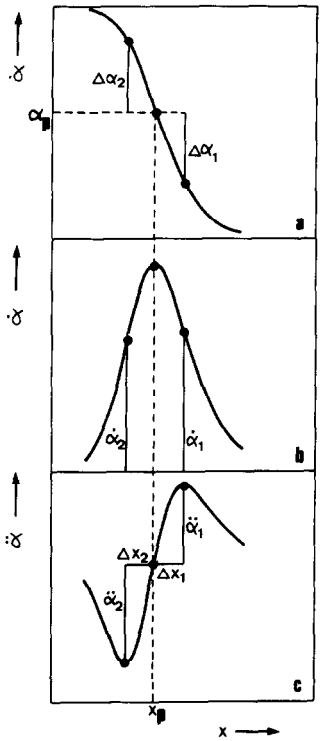

Fig. 1. Theoretical ITC (a), DTC (b) and DDTC (c) plotted against the reduced activation energy, showing the meaning of the inflexional asymmetry parameters.

An important feature of Δx_i is that it depends only on x_p and is invariant with respect to A and β. This provides a formulation of the $\Delta x_i(x_p)$ function representing each kinetic model as shown in Fig. 2. It should be pointed out that the $\Delta x_2(x_p)$ functions cannot be calculated for the D2, D4 and R0($n \leq \frac{1}{2}$) model because the second inflexion point of the DTC does not exist. It is seen from Fig. 2 that the DTC is significantly asymmetrical for $x_p < 15$. This is particularly evident in the case of the D3 and JMA($n < 1$) model. On the other hand, the difference between Δx_1 and Δx_2 becomes smaller with increasing x_p, and the corresponding DTC is almost symmetrical with respect to the reduced activation energy.

TABLE 2

The inflexional asymmetry parameters

Variable	Parameter
x	$\Delta x_i = \lvert x_i - x_p \rvert$
α	$\Delta \alpha_i = \lvert \alpha_i - \alpha_p \rvert$
$\dot{\alpha}$	$Q = \lvert \dot{\alpha}_1 / \dot{\alpha}_2 \rvert$
$\ddot{\alpha}$	$S = \lvert \ddot{\alpha}_1 / \ddot{\alpha}_2 \rvert$

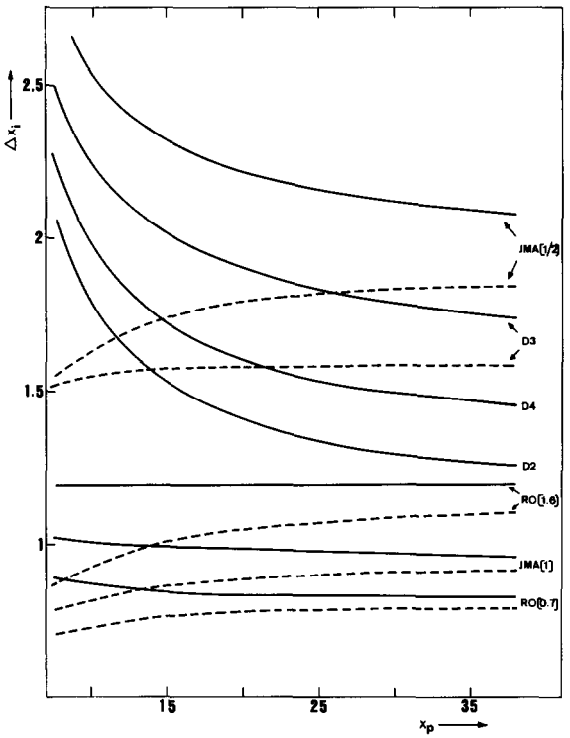

Fig. 2. The $\Delta x_1(x_p)$ dependence (solid lines) and $\Delta x_2(x_p)$ dependence (dashed lines) for the R0(n), JMA(n), D2, D3 and D4 models.

Figure 3 shows the $\Delta x_1(n)$ dependence for $x_p = 20$ corresponding to the R0(n) and JMA(n) models. This figure does not change substantially with x_p because Δx_1 is practically constant. It is noteworthy that the $\Delta x_i(n)$

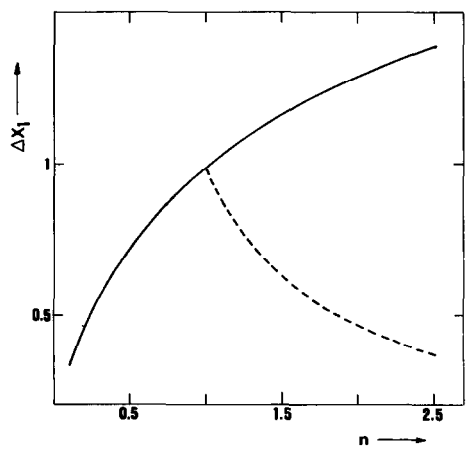

Fig. 3. The dependence of the parameter Δx_1 on the kinetic exponent for $x_p = 20$. The solid line and dashed line correspond to the R0(n) and JMA(n) models, respectively.

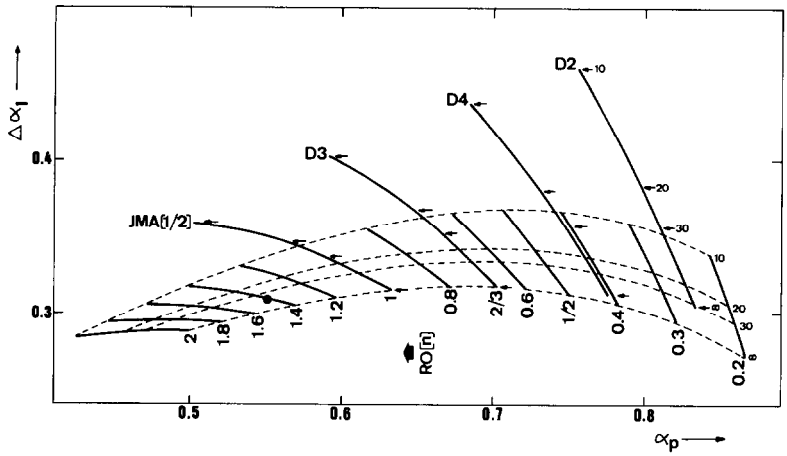

Fig. 4. The $\Delta\alpha_i(\alpha_p)$ diagram: the effect of x_p is shown by dashed lines for R0(n) and by arrows for JMA($\frac{1}{2}$), D3, D4 and D2 models ($x_p = 10, 20, 30, \infty$). The filled circle corresponds to the DTC shown in Fig. 1.

curves intersect at $n = 1$ because the R0(1) and JMA(1) models are identical.

It becomes apparent that both the $\Delta x_i(x_p)$ and $\Delta x_i(n)$ diagrams could be used in the kinetic analysis of the thermoanalytical curve. Nevertheless, their practical application is limited because the activation energy must be a priori known for the calculation of the Δx_i and x_p parameters.

The inflexional asymmetry of α

The inflexional asymmetry of the DTC with respect to the degree of conversion is defined by the parameter $\Delta\alpha_i$, formulated in Table 2. To calculate this parameter, the values of α_p and α_i are needed. These values can be determined by solving eqns. (6) and (7), respectively, using x_p and x_i calculated as described above.

It was found that both $\Delta\alpha_i$ and α_p depend only on x_p and are invariant with respect to A and β. For practical reasons it is useful, however, to combine $\Delta\alpha_i(x_p)$ and $\alpha_p(x_p)$ functions and construct $\Delta\alpha_i(\alpha_p)$ diagrams. These diagrams are depicted by full lines in Figs. 4 and 5 for the first and the second inflexion point, respectively. It is significant that there is a $\Delta\alpha_i(\alpha_p)$ curve for each kinetic model. The effect of x_p is clearly shown by dashed lines for the R0(n) model and by arrows for the JMA($\frac{1}{2}$) and diffusion models (D2, D3, D4). The upper ends of the $\Delta\alpha_i(\alpha_p)$ curves always correspond to $x_p = 10$ and the lower ones to $x_p = \infty$. In other words, with increasing x_p, the $\Delta\alpha_i$ decreases and α_p increases. This behaviour is more dramatic for the diffusion models than for the R0(n) model. In the case of the JMA(n) model, the influence of x_p decreases with increasing n.

From the foregoing discussion, it follows that the $\Delta\alpha_i(\alpha_p)$ diagram could be used for an estimation of the probable kinetic model from the DTC

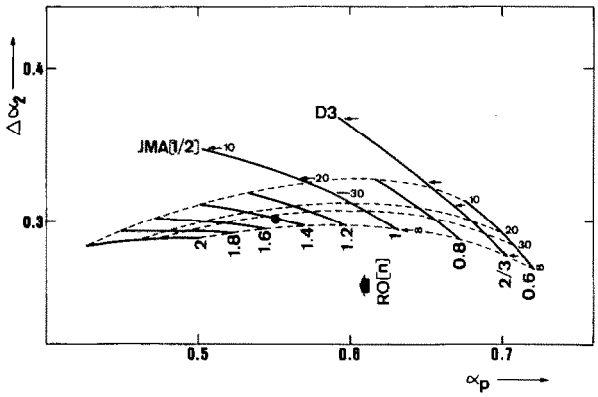

Fig. 5. The $\Delta\alpha_2(\alpha_p)$ diagram: the symbols are the same as in Fig. 4.

without any additional information. For example the data corresponding to Fig. 1 are $\alpha_p = 0.550$, $\Delta\alpha_1 = 0.310$ and $\Delta\alpha_2 = 0.301$. From a simple visual inspection (filled circles) of Figs. 4 and 5, it can be seen that the DTC curve in Fig. 1 corresponds well to the R0(1.4) model. It has not been possible to include in Fig. 5 the $\Delta\alpha_i(\alpha_p)$ curves of the D2 and D4 models for the reason discussed above. From this point of view, it seems that the $\Delta\alpha_1(\alpha_p)$ diagram is more useful for the kinetic analysis as it includes all the kinetic models discussed.

Of course there are some limitations. For example it is impossible to determine the kinetic exponent of the JMA(n) model by this method as the corresponding $\Delta\alpha_i(\alpha_p)$ curve is common to all values of n. It would also be difficult to distinguish between the following pairs of kinetic models: D2 and R0(0.25); D3 and R0($\frac{2}{3}$); D4 and R0(0.41). These values of the kinetic exponents, i.e. $n = 0.25$, $\frac{2}{3}$ and 0.41, respectively, are in good agreement with the apparent reaction orders proposed for the diffusion models by Criado et al. [8].

The inflexional asymmetry of $\dot{\alpha}$

The parameter Q describing the inflexional asymmetry of $\dot{\alpha}$ can be expressed analytically by combining the formula given in Table 2 with eqns. (2) and (3)

$$Q = \left| \frac{g(\alpha_1)f(\alpha_1)}{g(\alpha_2)f(\alpha_2)} \right| \left[\frac{x_1\pi(x_2)}{x_2\pi(x_1)} \right] \tag{8}$$

Taking into account that both $\Delta\alpha_i$ and Δx_i depend only on x_p, as has already been mentioned, the parameter Q can also be expressed as a function of x_p. The $Q(x_p)$ dependencies are shown in Fig. 6 for several kinetic models. The values of Q were calculated from eqn. (8) using the theoretical values of α_i and x_i (see above).

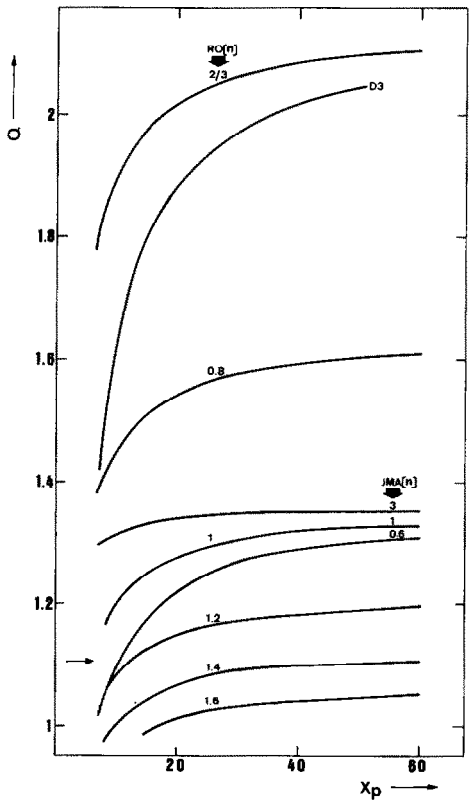

Fig. 6. The dependence of the parameter Q versus x_p for the R0(n), JMA(n) and D3 models. The arrow at the left-hand-side corresponds to the parameter Q of the DTC shown in Fig. 1.

It is seen that the parameter Q strongly depends on x_p, especially for $x_p < 20$. Its practical application in kinetic analysis is restricted, therefore, to those cases where the value of x_p is known. For example the DTC presented in Fig. 1 corresponds to $Q = 1.105$. This value is shown by the arrow at the left-hand-side of Fig. 6. It is clear that having only this information it is quite impossible to determine the kinetic model.

The inflexional asymmetry of $\ddot{\alpha}$

The inflexional asymmetry of $\ddot{\alpha}$ is expressed by the parameter S. This parameter, known as the shape index, was firstly formulated by Kissinger [9] in 1957. It was defined as the absolute value of the ratio of the slopes of the tangents to the DTA curve at the inflexion points, as is shown schematically in Fig. 7. From the formula given in Table 2 and eqn. (5) we can obtain an equivalent mathematical expression for the shape index

$$S = \left| \frac{f(\alpha_1)g(\alpha_1)[f'(\alpha_1)g(\alpha_1) + x_1\pi(x_1)]}{f(\alpha_2)g(\alpha_2)[f'(\alpha_2)g(\alpha_2) + x_2\pi(x_2)]} \right| \left[\frac{x_1\pi(x_2)}{x_2\pi(x_1)} \right]^2 \qquad (9)$$

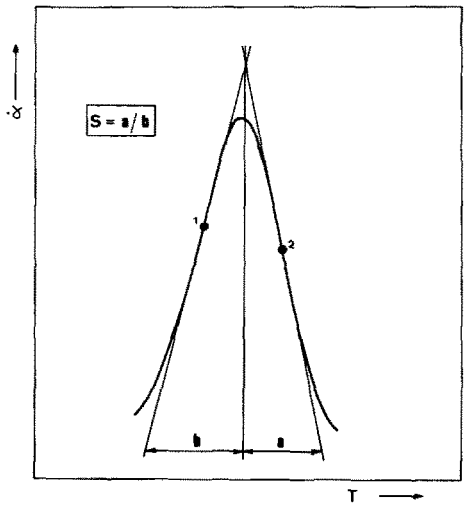

Fig. 7. Graphical method for the determination of the shape index from the DTC.

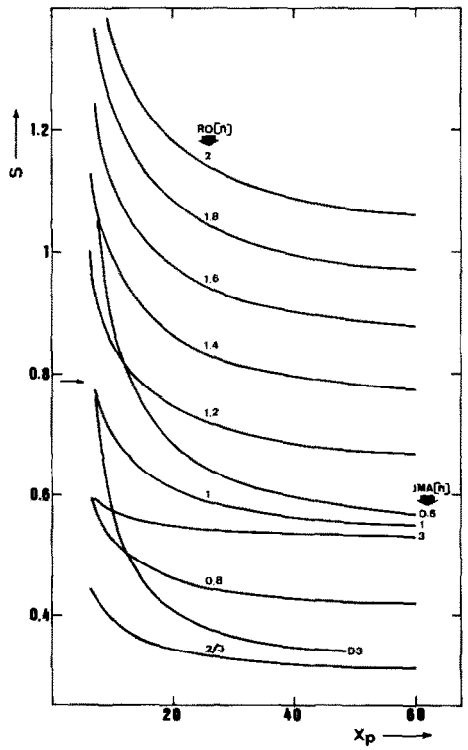

Fig. 8. The dependence of the shape index versus x_p for the R0(n), JMA(n) and D3 models. The arrow at the left-hand-side corresponds to the parameter S of the DTC shown in Fig. 1.

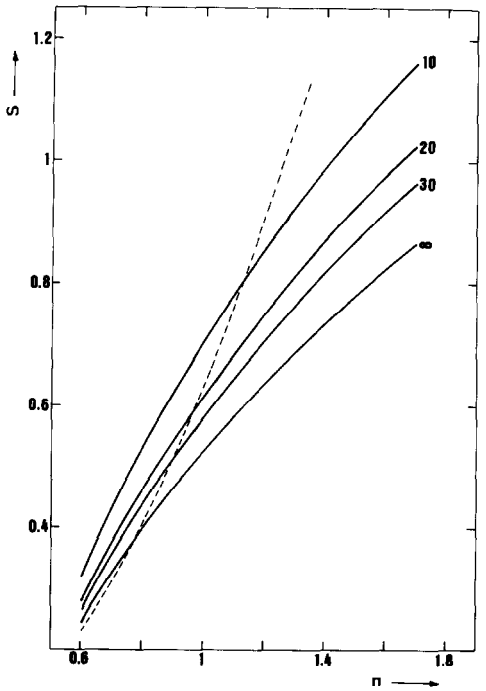

Fig. 9. The $S(n)$ plots for the R0(n) model (solid lines) calculated by eqn. (9). The numbers correspond to the values of x_p. The dependence proposed by Kissinger (see text) is shown by the dashed line.

In the context of the foregoing, the shape index can be expressed as a function of x_p. The $S(x_p)$ dependencies are shown in Fig. 8 for several kinetic models. The values of S were calculated from eqn. (9) using the theoretical values of α_i and x_i (see above).

It can be seen in Fig. 8 that the shape index decreases with increasing x_p for all kinetic models. In contrast, increasing $S(x_p)$ dependencies have been published in some earlier works [10–13]. These results were obtained under the assumption that $x_i \cong x_p$. It seems, therefore, that this approximation cannot be used and that all previous results are probably wrong.

Kissinger [9] suggested a simple relationship between the shape index and the kinetic exponent for the R0(n) model in the form $S = 0.63n^2$. This dependence is illustrated in Fig. 9 by the dashed line. The solid lines in Fig. 9 correspond to the $S(n)$ dependencies calculated correctly by the solution of eqn. (9) for various values of x_p. These curves are shifted downwards with increasing x_p. Thus it is evident, that the Kissinger relationship cannot be successfully used for the kinetic exponent because it does not take into account the influence of x_p.

The arrow at the left-hand-side of Fig. 8 corresponds to the shape index of the DTC shown in Fig. 1 ($S = 0.792$). It can be seen that in this case, also,

it is impossible to determine the kinetic model unless the value of x_p is known.

CONCLUSION

The results of this study show that the inflexional asymmetry parameters exhibit some interesting features which allow them to be applied in kinetic analysis. It was found, however, that the parameters Δx_i, Q and S do not result in a unique indicated kinetic model unless the parameter x_p and, thus, the activation energy are known. This is a common drawback for the use of these parameters in kinetic analysis in practice. On the other hand, the $\Delta\alpha_i(\alpha_p)$ diagram allows us, under certain circumstances, to estimate the kinetic model by the analysis of a single TC.

The sensitivity of this method depends, however, on the accuracy of the $\Delta\alpha_i$ and α_p values determined from the DDSC. This curve is usually obtained by numerical differentiation and smoothing of the ITC (TG curve) or DTC (DTA and DSC curves) and thus it strongly depends on the noise content of the original data. It is well known that each numerical smoothing leads to the distortion of the experimental data. The extent of this distortion must be known for any practical application of $\Delta\alpha_i(\alpha_p)$ diagrams.

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