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ANALYSIS OF THE SHAPE INDEX OF DTG OR DTA CURVES UNDER A HYPERBOLIC OR LOGARITHMIC SCHEDULE

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ABSTRACT

It is shown that the reacted fraction, αm, at the maximum reaction rate of solid state transformation analyzed under a hyperbolic or a logarithmic heating schedule depends only on the reaction mechanism—being independent of the actual value of E/RT. On the other hand, it has been demonstrated that the corresponding "shape index", S, defined as the slope ratio of the tangents to the DTG or DTA traces depends only on the reaction mechanism and does not depend either on E/RT or on the curve broadening.

The above statements are not accomplished if the DTG or DTA traces are obtained by means of a conventional linear heating program.

INTRODUCTION

Horowitz and Metzger [1] and other authors [2,3] have shown that the reaction order of thermal decomposition of solids can be determined from the value of the reacted fraction, αm, at the maximum reaction rate. This method has been developed in further papers [4] in order to allow the discrimination of the other kinetic models commonly used in literature [5] for describing solid state reactions. It has been concluded [4] that αm depends on both the reaction mechanism and the value of E/RT which can lead to a misinterpretation of the results.

On the other hand, we have developed a method to determine the mechanism of solid state reaction from the "shape index", S, of DTA or DTG curves, obtained under a constant heating rate. This method [6] is similar to that previously formulated by Kissinger [7] for determining the reaction order of homogeneous reaction. The parameter S is defined as the slope ratio of the tangents to the DTA or DTG trace at the inflection points, and may be expressed analytically as follows

$$S=\frac{(\mathrm{d}^2\alpha/\mathrm{d}t^2)_1}{(\mathrm{d}^2\alpha/\mathrm{d}t^2)_2}=\frac{a}{b} \tag{1}$$

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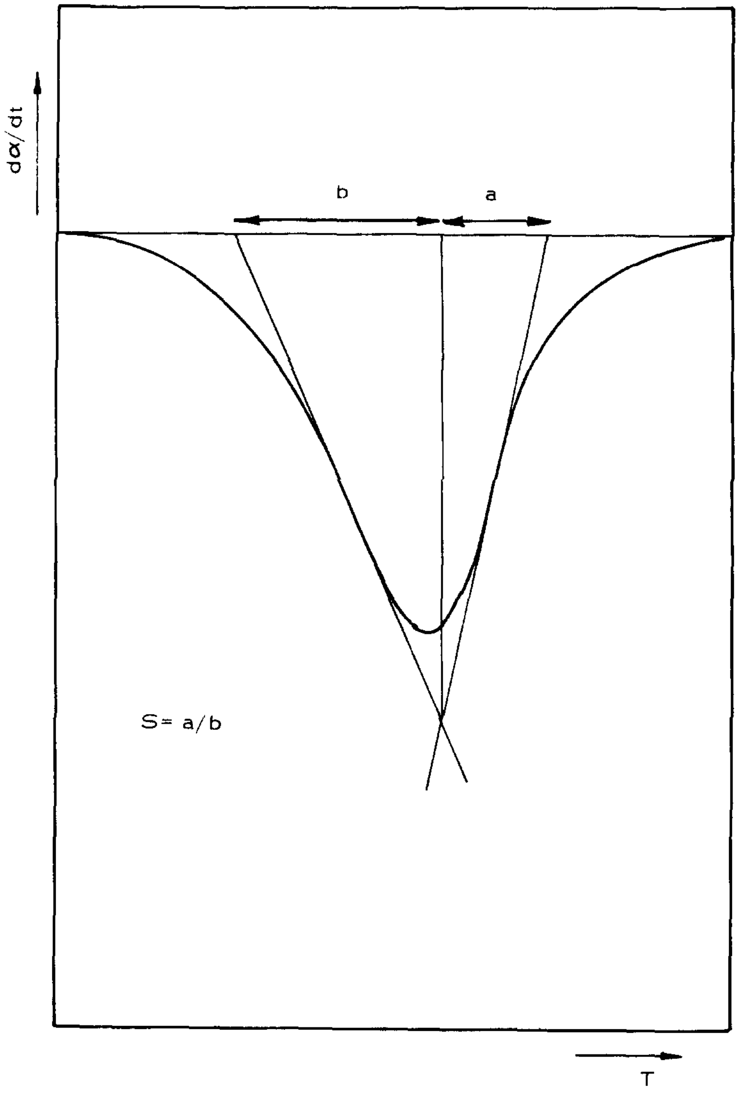

Fig. 1. "Shape index" of DTG curves.

where subscripts 1 and 2 refers to the first and second inflection points, respectively (i.e., where $d^3\alpha/dt^3 = 0$). The meaning of *a* and *b* is illustrated in Fig. 1.

It was reported in ref. 6 that *S* depends not only on the kinetic law but also on both the E/RT value and the DTG curve broadening. Therefore, it is rather difficult to determine the actual reaction mechanism from the "shape index" without any additional information.

The aim of the present paper is to extend the above method to the kinetic analysis of DTG curves recorded under a logarithmic or hyperbolic heating schedule. In this way we try to explore the possibility of overcoming the inconveniences found when the diagrams are recorded at a constant heating rate.

RESULTS AND DISCUSSION

The reaction rate of solid state transformations can be expressed by means of the general law

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

where α is the reacted fraction, T the absolute temperature, E the activation energy, A the pre-exponential factor, R the universal gas constant and $\mathrm{f}(\alpha)$ an algebraic function depending on the reaction mechanism.

In the case of a logarithmic temperature change, the temperature, T, is connected with the time, t, through the expression

$$-(1/T) = \ln t - a \tag{4}$$

a being a constant that can be arbitrarily selected. Equation (3) can be easily integrated giving

$$\mathrm{g}(\alpha) = \frac{AR}{E}\exp(-E/RT + a) \tag{5}$$

From eqns. (3) and (5) we obtain

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{E}{R}\frac{1}{\exp(a)}\mathrm{f}(\alpha)\mathrm{g}(\alpha) \tag{6}$$

from the differentiation of eqn. (6) we get, for the first derivative, after taking into account that $\mathrm{g}'(\alpha) = 1/\mathrm{f}(\alpha)$, the following expression

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2} = \frac{E}{R}\frac{1}{\exp(a)}[\mathrm{f}'(\alpha)\mathrm{g}(\alpha) + \mathrm{f}(\alpha)\mathrm{g}'(\alpha)]\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{7}$$

the value of $\alpha\mathrm{m}$ at which the maximum reaction rate is reached is defined by setting $\mathrm{d}^2\alpha/\mathrm{d}t^2$ equal to zero. From eqns. (6) and (7) we get, after rearranging terms, the expression

$$\mathrm{f}'(\alpha\mathrm{m})\mathrm{g}(\alpha\mathrm{m}) + 1 = 0 \tag{8}$$

the values of $\alpha\mathrm{m}$ calculated from eqn. (8) for each of the mechanisms quoted in Table 1 are shown in Table 2.

On the other hand, the inflection point occurs at an α value defined by setting the first derivative of eqn. (7) equal to zero. After rearranging we obtain

$$\mathrm{g}^2(\alpha i)\left[\mathrm{f}(\alpha i)\mathrm{f}''(\alpha i) + \mathrm{f}'^2(\alpha i)\right] + 3\mathrm{f}'(\alpha i) + 1 = 0 \tag{9}$$

TABLE 1

Algebraic expressions for the f(α), f′(α), f″(α) and g(α) functions corresponding to the most common mechanisms in solid state reactions

Mechanism	Symbol	f(α)	f′(α)	f″(α)	g(α)
Zero Order mechanism	R1	1	0	0	α
Phase boundary controlled reaction (Contracting Area)	R2	$(1-\alpha)^{1/2}$	$\frac{-1}{2(1-\alpha)^{1/2}}$	$\frac{-1}{4(1-\alpha)^{3/2}}$	$2[1-(1-\alpha)^{1/2}]$
Phase boundary controlled reaction (Contracting Volume)	R3	$(1-\alpha)^{2/3}$	$\frac{-2}{3(1-\alpha)^{1/3}}$	$\frac{-2}{9(1-\alpha)^{4/3}}$	$3[1-(1-\alpha)^{1/3}]$
Unimolecular decay law	F1	$(1-\alpha)$	-1	0	$-\ln(1-\alpha)$
Random Nucleation and Growth of nuclei (Avrami–Erofeev equation)	Am	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	$\frac{m\ln(1-\alpha)+m-1}{[-\ln(1-\alpha)]^{1/m}}$	$\frac{\frac{n-1}{n\ln(1-\alpha)}+(1-n)}{(1-\alpha)(-\ln(1-\alpha))}$	$[-\ln(1-\alpha)]^{1/m}$
One dimensional diffusion (Parabolic law)	D1	$1/2\alpha$	$\frac{-1}{2\alpha^2}$	$\frac{1}{\alpha^3}$	α^2
Two dimensional diffusion	D2	$1/(-\ln(1-\alpha))$	$\frac{-1}{[\ln(1-\alpha)]^2(1-\alpha)}$	$\frac{-2-\ln(1-\alpha)}{(1-\alpha)^2[\ln(1-\alpha)]^3}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three dimensional diffusion (Jander equation)	D3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$\frac{1/2-(1-\alpha)^{1/3}}{[1-(1-\alpha)^{1/3}]^2}.$	$\frac{3(1-\alpha)^{-1/3}-(1-\alpha)^{-2/3}-1}{3(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^3}$	$[1-(1-\alpha)^{1/3}]^2$
Three dimensional diffusion (Ginstein–Brounshtein equation)	D4	$\frac{3}{2[(1-\alpha)^{-1/3}-1]}$	$-\frac{(1-\alpha)^{-4/3}}{2[(1-\alpha)^{-1/3}-1]^2}$	$\frac{2((1-\alpha)^{1/3}-1)+1}{3(1-\alpha)^{8/3}[(1-\alpha)^{-1/3}-1]^3}$	$(1-\frac{2\alpha}{3})-(1-\alpha)^{2/3}$

TABLE 2

αm and S values of DTG curves recorded with either a hyperbolic or logarithmic heating schedule

Mechanism	αm	S
R1	1.000	–
R2	0.750	0.125
R3	0.703	0.300
F1	0.632	0.520
A2	0.632	0.520
A3	0.632	0.520
D1	1.000	–
D2	0.833	–
D3	0.703	0.300
D4	0.775	–

From eqns. (1), (6) and (7) the "shape index" of the DTG curves recorded under a logarithmic heating program can be expressed in the form

$$S = \frac{[f'(\alpha 1)g(\alpha 1) + 1]f(\alpha 1)g(\alpha 1)}{[f'(\alpha 2)g(\alpha 2) + 1]f(\alpha 2)g(\alpha 2)} \tag{10}$$

where $\alpha 1$ and $\alpha 2$ refer to the solutions of eqn. (9) at the first and second inflection points, respectively.

The values of the "shape index", S, calculated from eqn. (10) after taking into account the expressions of $f(\alpha)$, $g(\alpha)$, $f'(\alpha)$ and $f''(\alpha)$ given in Table 1 for each particular mechanism are also collected in Table 2. It is worthy of note to point out that in the case of the kinetic models of zero order (R1) and one dimensional diffusion (D1), the reaction rate increases continuously until the reagents are exhausted and, therefore, neither mathematical maximum nor inflection points were obtained from eqns. (8) and (9), respectively. However, the higher value of the reaction rate is reached at $\alpha = 1$ as shown in Fig. 2. Moreover it could be assumed that $S = 0$ according the "shape index" definition given in Fig. 1. With regard to the kinetic laws labeled Ra, two inflection points were obtained only for $n > 1/2$. Thus the value given in Table 2 for the "shape index", S, of reactions fitting a R2 ($n = 1/2$) model represents the limiting value of S when n tends to 1/2. Finally, no solutions were found for the reaction models D2 and D4.

In the case of a hyperbolic temperature change, T, is connected with time through the expression

$$\frac{1}{T} = \frac{1}{T_0} - bt \tag{11}$$

b being an arbitrarily chosen constant.

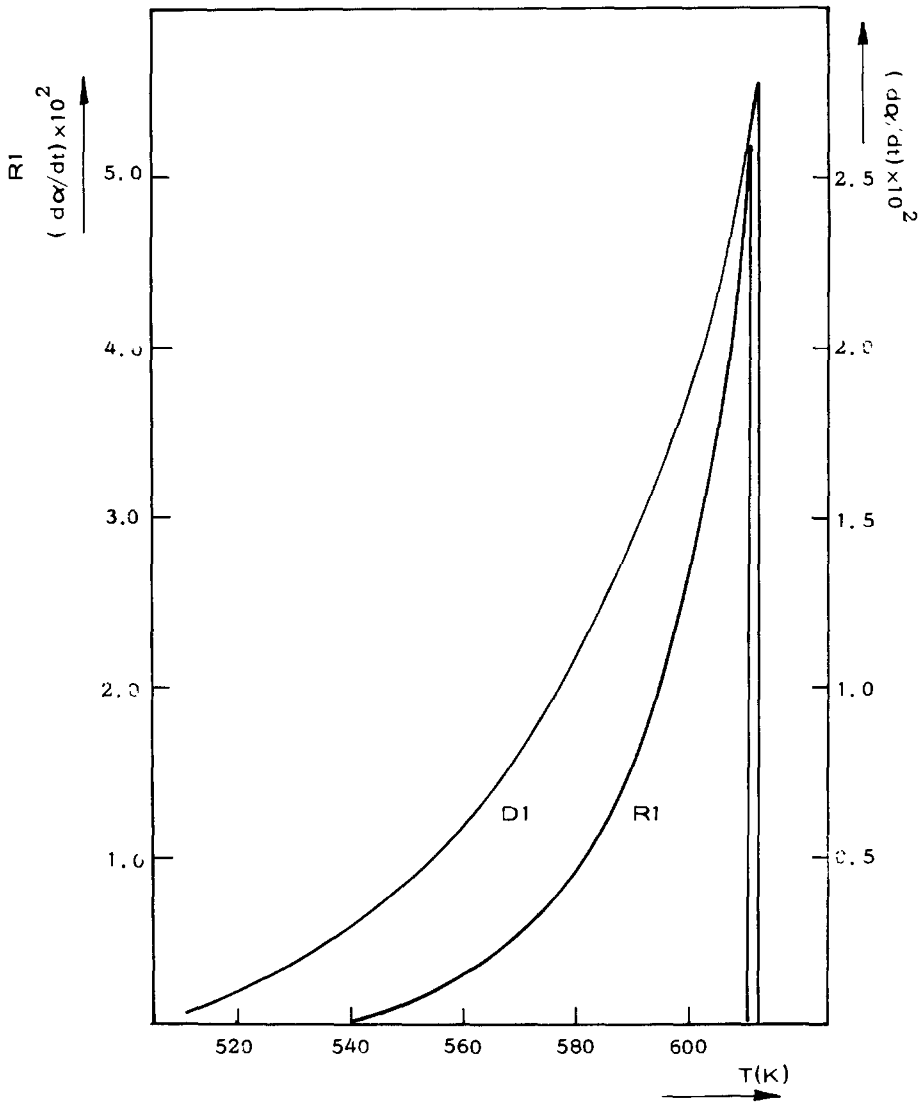

Fig. 2. Typical DTG curves corresponding to R1 and D1 mechanisms, calculated assuming a logarithmic heating program ($a = 12.8$) and the following kinetic parameters: $E = 167$ kJ mol^{-1} and $A = 10^{13}$ min^{-1}.

Following the calculation method used above we find that αm, αi and S values of a DTG or DTA curve recorded under a hyperbolic heating schedule also fulfil the conditions given by eqns. (8), (9) and (10), respectively.

The results reported in this paper shows that αm and S values of DTG or DTA curves recorded under a logarithmic or a hyperbolic heating program are independent of both E/RT and the broadening of the diagrams, contrary to previous reports concerning a linear heating program.

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