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Note

IS THE ŠESTÁK–BERGGREN EQUATION A GENERAL EXPRESSION OF KINETIC MODELS?

JIŘÍ MÁLEK * and JOSÉ M. CRIADO

Institute of Material Science, C.S.I.C. (Czechoslovakia) and University of Seville, 41 071 Seville (Spain)

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Many works are concerned with the kinetic analysis of thermoanalytical (TA) data [1]. The main problem of empirical kinetics is usually associated with the formulation of the so-called kinetic model, i.e. the $f(\alpha)$ function in the kinetic equation

$$d\alpha/dt = A \exp(-E/RT) f(\alpha) \quad (1)$$

The most frequently cited kinetic models are summarized in Table 1. The parameters A and E in eqn. (1) are characteristic constants that represent the kinetic process.

It is believed [1] that the Šesták–Berggren equation can be considered as a general expression for kinetic models. This equation undoubtedly includes, for example, the models JMA(1) ≡ SB(0, 1) and RO(n) ≡ SB(0, n) but it is not so evident for the D2, D3, D4 or JMA ($n \neq 1$) models. We have recently discussed this problem for constant rate thermal analysis [2] but as far as we

TABLE 1

Kinetic models

Model	Symbol	$f(\alpha)$
Šesták–Berggren eqn.	SB(m, n)	$\alpha^m (1-\alpha)^n$
Johnson–Mehl–Avrami eqn.	JMA(n)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
Reaction order eqn.	RO(n) [a]	$(1-\alpha)^n$
Two-dimensional diffusion	D2	$1/[-\ln(1-\alpha)]$
Jander eqn.	D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{2/3}]$
Ginstling–Brounshtein eqn.	D4	$3/2[(1-\alpha)^{-1/3}-1]$

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

* Permanent address: Joint Laboratory of Solid State Chemistry of the Czechoslovak Academy of Sciences and Institute of Chemical Technology, Náměstí legií 565, CS-532 10 Pardubice, Czechoslovakia.

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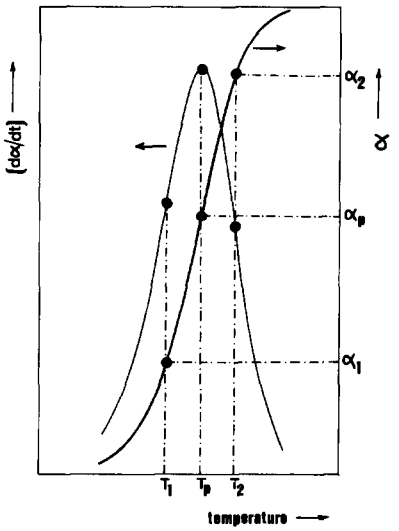

Fig. 1. Typical TA peak and the corresponding integral curve.

know it has not previously been sufficiently analysed for classical TA techniques.

Figure 1 shows a typical TA curve and its corresponding integral form. There are several important points which can be found on these curves, i.e. the maximum of the TA peak (T_p, α_p) and one or two inflection points (T_i, α_i) where $i = 1, 2$. All these points can be calculated [3] by numerical

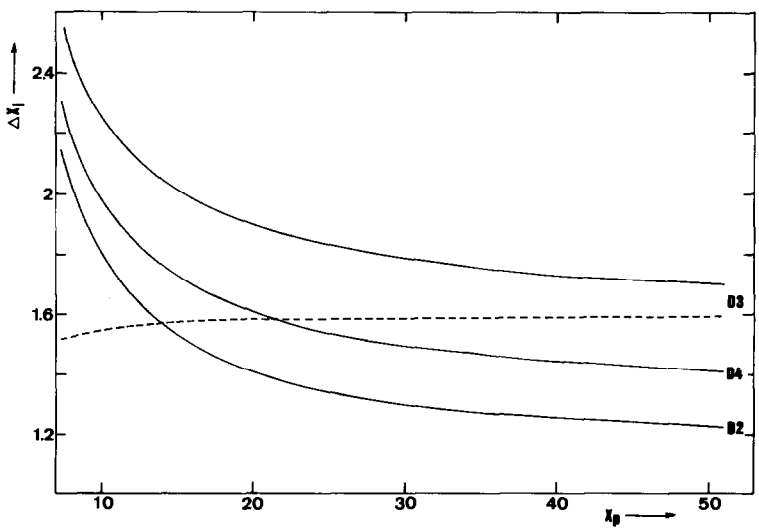

Fig. 2. The $\Delta x_i(x_p)$ dependence for D2, D3 and D4 models. The solid lines correspond to $i = 1$ and the dashed one to $i = 2$.

solution of eqn. (1). For practical reasons it is convenient to introduce a new variable, $x = E/RT$, called the *reduced activation energy*. We can now define the inflectional width of the first ($i = 1$) and second ($i = 2$) part of the TA peak by the parameter $\Delta x_i = |x_p - x_i|$. An interesting feature of this parameter is that it depends only on the value of x_p for each particular model, as shown in Fig. 2 for D2, D3 and D4 (diffusion) models, and it is invariant with respect to the kinetic parameters A and E. (The $\Delta x_2(x_p)$

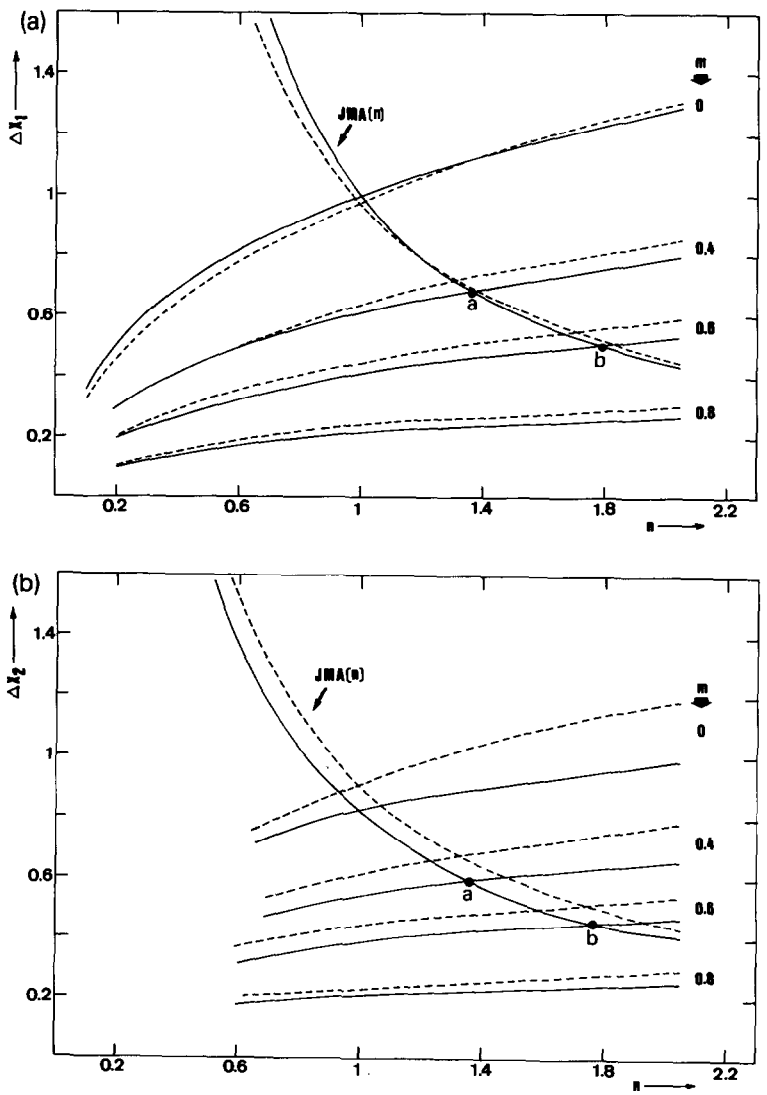

Fig. 3. The $\Delta x_i(n)$ plot for the SB(m, n) and JMA(n) models, $i = 1$ (a) and $i = 2$ (b). The solid lines correspond to $x_p = 10$ and the dashed ones to $x_p = 30$.

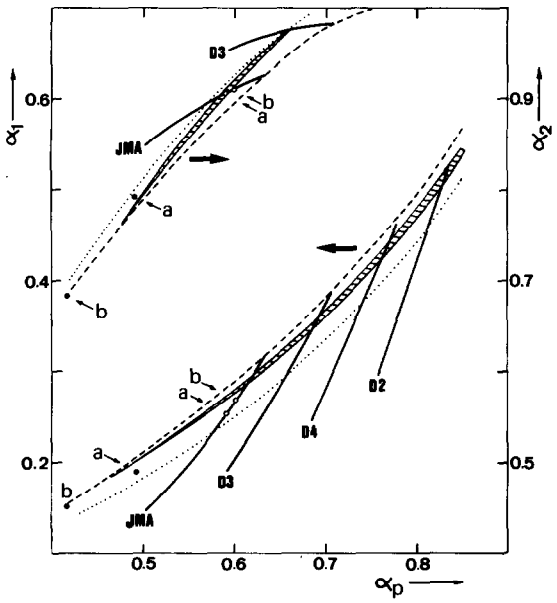

Fig. 4. The $\alpha_i(\alpha_p)$ diagram for $x_p > 10$. The solid lines correspond to the D2, D3, D4, R2, R3 and JMA(n) models, the area between the dotted ($x_p = \infty$) and dashed ($x_p = 10$) lines to the SB(0, n) model, and the shaded area to the SB(0.8, n) model.

function cannot be calculated for the D2 and D4 models as the second inflection point does not exist.)

It is noteworthy that $\Delta x_1 > \Delta x_2$ for the RO(n), JMA(n) and D3 models. Therefore, the corresponding TA peaks are asymmetric with respect to the reduced activation energy. This asymmetry is more significant for low values of x_p but it is not higher than 10% for $x_p > 30$.

For the models with a variable kinetic exponent, n, it is possible to plot the $\Delta x_i(n)$ dependence as shown in Fig. 3 for $x_p = 10$ (solid line) and $x_p > 30$ (dashed line). It can be seen that the Δx_i parameter for the SB($m < 1$, n) model is always lower than for the JMA($n < 1$). (It has been shown earlier [4] that physically acceptable values of the kinetic exponent, m, in the Šesták–Berggren equation should be lower than one.) On the other hand, the $\Delta x_i(n)$ curves cross at various points for the SB(m, n) and JMA ($n \geq 1$) models.

Another interesting diagram is depicted in Fig. 4 where each kinetic model is represented by an $\alpha_i(\alpha_p)$ line as shown for the JMA(n) and diffusion models. The upper end of the $\alpha_i(\alpha_p)$ line corresponds to $x_p = \infty$, and the lower to $x_p = 10$. These two limits are marked for the SB(0, n) model by dashed and dotted lines, respectively. Hence, the range of acceptable α_i and α_p values for this model is confined to the enclosed area. The area also includes part of the $\alpha_i(\alpha_p)$ line of the JMA(n) model for $n \geq 1$ and the remaining part outside this area corresponds to $1 > n \geq 1/2$. Analo-

gously, the $\alpha_i(\alpha_p)$ lines of the diffusion models are partially overlapped by the area for the following values of the kinetic exponent, n: 0.25 (D2), 2/3 (D3) and 0.41 (D4) if $x_p \in (23, \infty)$. This overlap region is further reduced for $m > 0$ for the SB(0.8, n) model as shown in Fig. 4 by the shaded area.

If we compare, however, the inflectional width of the TA peaks corresponding to the SB(m, n) and diffusion models (see Figs. 2 and 3) we can see that the parameter Δx_i for the diffusion models is almost double. Therefore, it seems that diffusion kinetic models cannot be successfully substituted by the SB(0, n) model for a fixed value of activation energy. On the other hand, as we have mentioned above, there are several intersections of $\Delta x_i(n)$ lines representing the SB(m, n) and JMA ($n \geq 1$) models (e.g. points a and b in Fig. 2) and thus the corresponding TA peaks have the same inflectional width. Nevertheless, the parameters α_i and α_p differ for both the SB(m, n) and JMA(n) models as shown in Fig. 4 by the filled and open circles, respectively.

Therefore, taking into account the results presented we can answer the question posed in the title of this note by concluding that the Šesták–Berggren kinetic equation cannot be considered as a general expression of the D2, D3, D4 and JMA($n \neq 1$) kinetic models for fixed values of activation energy.

ACKNOWLEDGEMENT

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