Thermochimica Acta, 158 (1990) 205–213
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE APPLICABILITY OF THE ŠESTÁK–BERGGREN KINETIC EQUATION IN CONSTANT RATE THERMAL ANALYSIS (CRTA)

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(Received 10 July 1989)

ABSTRACT

The applicability of the Šesták–Berggren (SB) formal kinetic model in CRTA is discussed with respect to the most common kinetic models in solid state kinetics. It was found that the CRTA curves for both the SB and Johnson–Mehl–Avrami (JMA) models exhibit similarities with respect to maxima or inflex points.

It has been shown that the experimental CRTA and TG data of the decomposition of nickel nitrate can be described by both the SB and JMA models. It seems, however, that the SB model is more suitable for a quantitative description of the process studied.

INTRODUCTION

The reaction rate ($\dot{\alpha}$) of a solid state process is frequently described by a kinetic equation of the form

$$\dot{\alpha} = A\, e^{-x} f(\alpha) \tag{1}$$

where x is the reduced activation energy ($x = E/RT$). The goal of empirical kinetics is to find an $f(\alpha)$ function fulfilling the mathematical requirements of eqn. (1). Besides the kinetic models derived from the geometry of a reacting interface, there are also formal expressions of the $f(\alpha)$ function which correlate as close as possible with the experimental data.

Almost twenty years ago, Šesták and Berggren [1] proposed an empirical kinetic model of the form

$$f(\alpha) = \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^r \tag{2}$$

It was believed [1,2] that this kinetic equation, containing three exponential terms, would provide a general expression for all the kinetic equations used for mathematical modelling of solid state reactions. Further mathematical

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0040-6031/90/$03.50

analysis [3] of eqn. (2) has shown, however, that no more than two kinetic exponents are necessary for the description of any experimental curve. Thus, after eliminating the third exponential term in eqn. (2), the final form obtained is

$$f(\alpha) = \alpha^m (1-\alpha)^n \tag{3}$$

It should be pointed out, however, that the exponential factors m and n in this Šesták–Berggren (SB) kinetic model have purely empirical significance and cannot be considered as universal constants for solid state reactions.

The aim of this paper is to discuss in detail the properties and limits of the SB model in CRTA with respect to the application of other models used in solid state kinetics. In addition, an attempt is made to calculate the formal kinetic parameters for the decomposition of nickel nitrate measured by CRTA and to compare these results with the classical thermogravimetric (TG) measurement.

THEORETICAL ASPECTS

The function $f(\alpha)$ defined by eqn. (3) has a maximum (α_M) and inflex points (α_{i1}, α_{i2}) defined by the following equations [4]

$$\alpha_M = \frac{m}{m+n} \quad \text{for } m,\ n > 0 \tag{4}$$

$$\alpha_{i1,\,i2} = \frac{m \pm [mn/(m+n-1)]^{1/2}}{m+n} \quad \text{for } m+n > 1 \tag{5}$$

It can be shown [4] that the conditions for the existence of inflex points within the acceptable limits of α can be formulated as follows

$$m \geq 1 \Leftrightarrow \alpha_{i1} \in \langle 0,\ \alpha_M \ ) \tag{6a}$$

$$n \geq 1 \Leftrightarrow \alpha_{i2} \in (\alpha_M,\ 1\ \rangle \tag{6b}$$

For the CRTA technique, we can write eqn. (1) in the form

$$v = A\ \mathrm{e}^{-x} f(\alpha) \tag{7}$$

where v is the constant reaction rate. By differentiating this equation with respect to α, we obtain the conditions for minima (α_m) and inflex point (α_i) of the CRTA curve [5]

$$\frac{\mathrm{d}T}{\mathrm{d}\alpha} = -\frac{T}{x}\frac{f'(\alpha_M)}{f(\alpha_M)} = 0 \tag{8}$$

$$\frac{\mathrm{d}^2T}{\mathrm{d}\alpha^2} = \frac{T}{x}[f(\alpha_i)]^{-2}\left\{[f'(\alpha_i)]^2\left(\frac{2}{x}+1\right) - f(\alpha_i)f''(\alpha_i)\right\} = 0 \tag{9}$$

TABLE 1

The values of α_M and α_i of the CRTA curves for the most frequently used kinetic models

Model	$f(\alpha)$	α_M	α_i
JMA [a]	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	$1-e^{(1-n)/n}$	–
SB [b]	$\alpha^m(1-\alpha)^n$	$m/(m+n)$	–
RO	$(1-\alpha)^n$	–	–
D2	$1/[-\ln(1-\alpha)]$	–	$1-e^{(2/x-1)}$
D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	–	$1-\{(8/x+6)/[4/x+5+(4/x+7)^{1/2}]\}^3$
D4	$3/2[(1-\alpha)^{-1/3}-1]$	–	$1-[(2+3x)/4x]^3$

[a] Valid for $n>1$.

[b] Valid for m, $n>0$.

Solution of eqn. (8) does not depend on the value of the reduced activation energy x. For the Johnson–Mehl–Avrami (JMA) and SB models, it is identical with the condition for the maximum of the $f(\alpha)$ function. On the other hand, the inflex point of the CRTA curve generally depends on x. The mathematical conditions for the minima ($0<\alpha_M<1$) and inflex point ($0<\alpha_i<1$) are summarised in Table 1 for the most common models used in solid state kinetics. It is noteworthy, however, that there is no inflex point in the interval $\alpha \in (0, 1)$ for the CRTA curves of both the JMA and SB models. This result indicates that the SB model cannot be successfully used as a general expression for diffusion models (D2, D3 and D4).

From the above it is clear that there is a similarity, with respect to α_M and α_i, between CRTA curves for the JMA and SB kinetic models. We will thus focus our attention on examining the applicability of these models to the quantitative description of the CRTA experimental data.

EXPERIMENTAL

$Ni(NO_3)_2 \cdot 6H_2O$, Panreac, AnalaR, was used for the decomposition study. The anhydrous salt was prepared by dehydrating the corresponding hexahydrate in situ at 150 °C. The total weight loss after this treatment agrees well with that expected for the conversion of hexahydrate to anhydrous nickel nitrate.

Both the CRTA and TG experiments were performed in a Cahn RG electrobalance model 2000 using approximately 15 mg of the sample. The thermocouple was installed close to the sample. For the CRTA measurements, the apparatus was modified in order to monitor the furnace temperature in such a way that the total decomposition rate remains constant over the decomposition range. This was assured both by controlling the residual pressure in the close vicinity of the sample and by maintaining a constant pumping rate, which can be selected by means of a valve.

RESULTS AND DISCUSSION

Typical CRTA experimental curves for nickel nitrate decomposition are shown in Fig. 1. It is clear that all these T–α plots have minima at α_M. The α_M values and the programmed decomposition velocity are summarised for each curve in Table 2.

It has recently been demonstrated [5,6] that nickel nitrate decomposition obeys the JMA kinetic equation. Knowing the values of α_M, the parameter n for the JMA model is given by [7,8] *

$$n = \frac{1}{1 + \ln(1 - \alpha_M)} \tag{10}$$

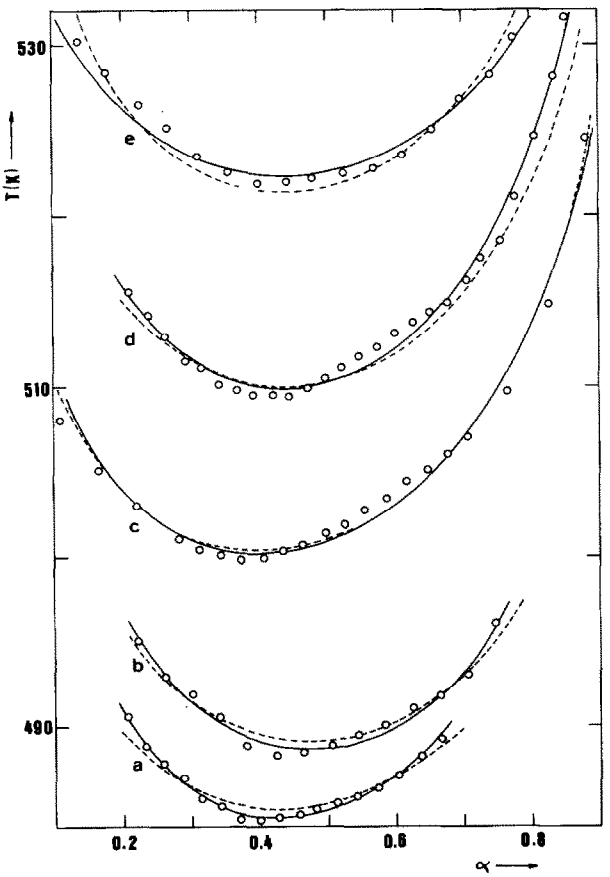

Fig. 1. Comparison between the experimental CRTA data (○), corresponding to nickel nitrate decomposition, and the theoretical curves based on both the SB model (———) and the JMA model (– – –).

* Equations (10) and (13) were derived using the conditions for the minimum of the CRTA curve (see Table 1) for the JMA and SB models, respectively.

TABLE 2

The values of the decomposition velocity and of α_M for the experimental CRTA curves presented in Fig. 1

Curve	v (min^{-1})	α_M
a	1.45×10^{-3}	0.433
b	2.03×10^{-3}	0.475
c	5.03×10^{-3}	0.400
d	6.44×10^{-3}	0.440
e	7.03×10^{-3}	0.439

Assuming the activation energy value to be $E = 84$ kJ mol^{-1} [6], the values of the reduced activation energy x_j can be calculated for all the experimental points. Then, the pre-exponential term in eqn. (7) may be expressed as

$$A = \frac{1}{q}\sum_{j=1}^{q}\frac{v\ e^{x_j}}{f(\alpha_j)} \tag{11}$$

where the subscript j corresponds to an arbitrary experimental point and q is the number of experimental points.

All calculated kinetic parameters for the JMA model are summarised in Table 3. Except for curve b, the values of the kinetic exponent are close to 2, which agrees with the results obtained from both isothermal and non-isothermal TG measurements [6]. The calculated T–α curves are shown in Fig. 1 by broken lines. Equation (7) can be rewritten for the SB model in the form

$$x_j = \ln(A/v) + n\ \ln\left[\alpha_j^p(1-\alpha_j)\right] \tag{12}$$

where the exponent p corresponds to the ratio of the kinetic parameters ($p = m/n$), calculated using the equation

$$p = \alpha_M/(1-\alpha_M) \tag{13}$$

for the values of α_M given in Table 2. Figure 2 shows the linear dependen-

TABLE 3

Calculated kinetic parameters for the JMA kinetic model

Curve	n	A (min^{-1})
a	2.31	1.69×10^{6}
b	2.81	1.70×10^{6}
c	2.04	3.40×10^{6}
d	2.38	2.78×10^{6}
e	2.37	1.89×10^{6}

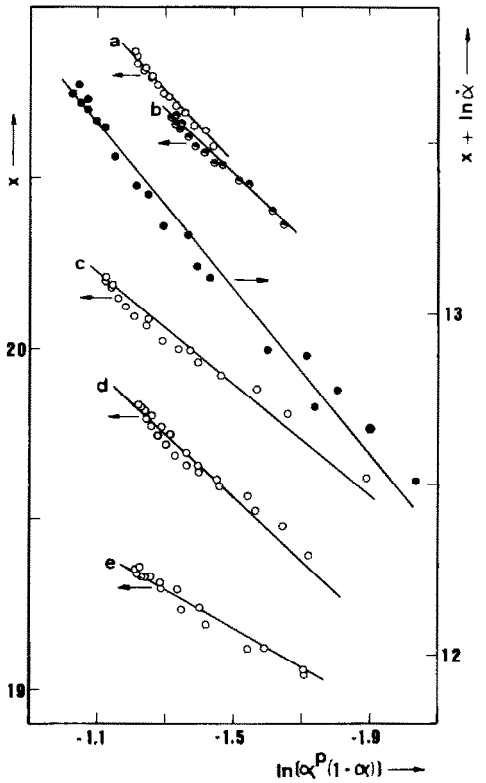

Fig. 2. ○ and ⊖, The dependencies of x vs. $\ln(\alpha^p(1-\alpha))$ for the CRTA data (see Fig. 1, curves a–e); ●, the dependence of $x + \ln \dot{\alpha}$ vs. $\ln[\alpha^p(1-\alpha)]$ for the TG data (see inset of Fig. 3).

cies of x_j versus $\ln[\alpha_j^p(1-\alpha_j)]$ for all the CRTA experimental curves. The kinetic parameter n for the SB model corresponds to the slope of these lines. The parameter m is then given by $m = pn$ and the pre-exponential factor is calculated using eqn. (11).

The kinetic parameters for the SB model are summarised in Table 4. Theoretical T–α curves, calculated using these parameters, are shown in Fig. 1 by full lines. Taking into account experimental errors, both calculated and

TABLE 4

Calculated kinetic parameters for the SB kinetic model

Curve	m	n	A (min^{-1})
a	0.81	1.06	5.92×10^6
b	0.83	0.92	6.50×10^6
c	0.54	0.81	7.40×10^6
d	0.73	0.93	8.18×10^6
e	0.45	0.57	3.57×10^6

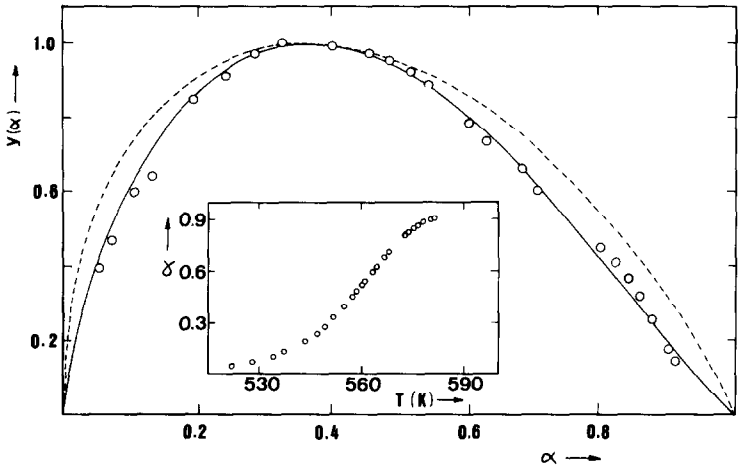

Fig. 3. The theoretical $y(\alpha)$, functions calculated using eqn. (15) for both the SB (———) and JMA models (– – –). ○, Experimental data transformed by eqn. (14). The inset shows the TG data for nickel nitrate decomposition.

experimental CRTA curves are in acceptable agreement. For experimental curve c, the calculated dependencies for both the JMA and SB models are practically identical. For all other experimental curves, the SB model fits the experimental data better. This higher flexibility of the SB kinetic model has been demonstrated in a description of the crystallisation kinetics of chalcogenide glasses [9].

It is interesting to compare the results of the CRTA measurements with a kinetic analysis of the TG data. The experimental data for nickel nitrate decomposition measured at the heating rate $\beta = 3$ K min^{-1} are shown in the inset of Fig. 3.

We can define the function $y(\alpha_j) \in \langle 0, 1 \rangle$, which is characteristic of the particular kinetic model, as follows

$$y(\alpha_j) = \frac{\dot{\alpha}_j \, e^{x_j}}{y_{max}} \tag{14}$$

where y_{max} corresponds to the maximum value of the $y(\alpha)$ function. Therefore, from eqn. (1), for both the JMA and SB models

$$y(\alpha_j) = f(\alpha_j)/f(\alpha_M) \tag{15}$$

The experimental TG data transformed using eqn. (14) are shown in Fig. 3. From eqn. (15), it is clear that the maximum of the $y(\alpha)$ curve corresponds to the maximum of the function $f(\alpha)$. It was found that $\alpha_M = 0.36$. Using this value, the parameter n for the JMA model can simply be calculated using eqn. (10). The parameter p for the SB model may be determined as described above for the CRTA data. Equation (1) can be rewritten after

TABLE 5

Kinetic parameters calculated from TG data

Model	m	n	A (min^{-1})
JMA	–	1.81	5.70×10^6
SB	0.68	1.20	1.87×10^6

converting it to logarithms in the following form [8]

$$x_j + \ln \dot{\alpha}_j = \ln A + n \ln\left[\alpha_j^p (1 - \alpha_j)\right] \tag{16}$$

Thus the slope of the dependence $x_j + \ln \dot{\alpha}_j$ versus $\ln[\alpha_j^p(1 - \alpha_j)]$ gives the value of the parameter n for the SB model. Its dependence is shown in Fig. 2. Knowing the values of the kinetic exponents, the $y(\alpha)$ functions for both the JMA and SB models can be calculated using eqn. (15). These functions are compared with the experimental data in Fig. 3. It is clear that, as with the CRTA curves, the SB kinetic model is in better agreement with the experimental data. The pre-exponential factor for both kinetic models is given by

$$A = \frac{1}{q} \sum_{j=1}^{q} \frac{\dot{\alpha}_j e^{x_j}}{f(\alpha_j)} \tag{17}$$

All the kinetic parameters calculated from the TG data for the JMA and SB models are shown in Table 5.

To summarise, the following conclusions can be drawn. If the CRTA curve exhibits a minimum, it can be described by both the JMA and SB models. It has been shown, however, that the SB model allows a more quantitative description of the CRTA and TG experimental data for the decomposition of nickel nitrate.

ACKNOWLEDGEMENT

This work was partially supported by a grant from the Spanish Ministry of Education and Science.

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