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Thermochimica Acta 254 (1995) 147–152

thermochimica acta

The problem of discerning Avrami–Erofeev kinetic models from the new controlled rate thermal analysis with constant acceleration of the transformation

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Received 30 September 1993; accepted 19 August 1994

Abstract

A new experimental arrangement, a variation on controlled rate thermal analysis (CRTA), with constant acceleration of the transformation has been proposed. It has been theoretically proved that the new technique supplies more information than the conventional CRTA method for discriminating between solid state transformations following an Avrami–Erofeev kinetic model.

Keywords: Avrami–Erofeev; CRTA; Kinetics; Model

1. Introduction

Controlled rate thermal analysis (CRTA) is a general method of thermal analysis developed by Rouquerol [1]. This thermoanalytical approach makes use of the same measuring devices as conventional thermal analysis, but the operation is basically different, the temperature of the sample being monitored in such a way that the reaction rate is maintained constant. It has been shown in previous papers [2,3] that this method allows better discrimination between the kinetic models of solid state reactions than conventional TG.

It has previously been proved [4] that a mere glance at the shape of CRTA curves provides an easy way of discriminating between "n-order", Avrami–Erofeev and diffusion kinetic models; in particular, the shape of Avrami–Erofeev $\alpha - T$ curves is

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SSDI 0040-6031(94)02068-X

very characteristic, which is an interesting and special feature of the CRTA approach. However, the differences in behaviour within the Avrami–Erofeev kinetic family ($n = 1.5$; 2; 2.5; 3; 4) are very small and it would be difficult to select unambiguously the correct mechanism. In order to overcome this difficulty we propose a new experimental arrangement, CRTA with constant acceleration of the transformation, that supplies more information than the constant rate CRTA method for discerning Avrami–Erofeev kinetic models. The new procedure can be considered as a new application of the CRTA method that implies a reaction rate which increases linearly with time (i.e. $Ct = \mathrm{d}\alpha/\mathrm{d}t$).

2. Theoretical

2.1. Kinetic analysis of CRTA curves recorded with constant acceleration of the transformation

It is well known that the rate of a solid state reaction obeying the Avrami–Erofeev kinetic law [5,6] is given by the general expression

$$\mathrm{d}\alpha/\mathrm{d}t = An(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}\exp(-E/RT) \quad (1)$$

where A is the pre-exponential factor, E is the activation energy and R is the molar gas constant. Table 1 summarizes the values of the parameter n which may be obtained for various boundary conditions. If the thermoanalytical curve is obtained at a constant decomposition rate $C = \mathrm{d}\alpha/\mathrm{d}t$, we have the constant rate CRTA approach, but if the reaction rate is taken as a linear function of time (i.e. $Ct = \mathrm{d}\alpha/\mathrm{d}t$) instead of remaining constant, then

$$\mathrm{d}\alpha/\mathrm{d}t = Ct \quad (2)$$

where C is a constant arbitrarily selected by the user. By rearrangement and integration, Eq. (2) becomes

$$\mathrm{d}\alpha/\mathrm{d}t = (2C)^{1/2}\alpha^{1/2} \quad (3)$$

From Eqs. (1) and (3) we get

$$\frac{\alpha^{1/2}}{n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}} = \frac{A}{(2C)^{1/2}}\exp(-E/RT) \quad (4)$$

Table 1

Kinetic model	Phase boundary controlled	Diffusion controlled
Three-dimensional growth	4	2.5
Two-dimensional growth	3	2
One-dimensional growth	2	1.5

Taking logarithms we can write

$$\ln \alpha^{1/2} - \ln[n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}] = \ln \frac{A}{(2C)^{1/2}} - \frac{E}{RT} \quad (5)$$

It has been shown [4] that the analysis of the shape of a constant rate CRTA curve provides valuable information for elucidating the actual kinetic law obeyed by the reaction, but it is difficult to discriminate the coefficient n of the Avrami–Erofeev kinetic model. Therefore it was considered of interest to carry out a comparison between constant rate CRTA and this new *time-dependent* CRTA in order to discriminate between the various Avrami–Erofeev kinetic models.

Eqs. (6) and (7) represent the first and second derivatives of T with respect to α as obtained from Eq. (4):

$$\frac{dT}{d\alpha} = \frac{RT^2}{E}\left[\frac{1}{2\alpha} - \frac{n\ln(1-\alpha)+n-1}{n(1-\alpha)[-\ln(1-\alpha)]}\right] \quad (6)$$

$$\frac{d^2T}{d\alpha^2} = \frac{RT^2}{E}\left[\frac{2RT}{E}\left(\frac{1}{2\alpha} - \frac{n\ln(1-\alpha)+n-1}{n(1-\alpha)[-\ln(1-\alpha)]}\right)^2 - \frac{1}{2\alpha^2} + \frac{n\ln(1-\alpha)^2+(n-1)\ln(1-\alpha)+n-1}{n(1-\alpha)^2\ln(1-\alpha)^2}\right] \quad (7)$$

The value of α at which there is a maximum or a minimum (α_m) is defined by setting Eq. (6) equal to zero, i.e.

$$\frac{n\ln(1-\alpha_m)+n-1}{n(1-\alpha_m)[-\ln(1-\alpha_m)]} = \frac{1}{2\alpha_m} \quad (8)$$

The sign of Eq. (7) after substituting in the α_m value calculated from Eq. (8) can be used as a criterion for discerning maxima or minima. Solutions of Eq. (8) have only been found for kinetic models with $n > 2$. These solutions are given in Table 2. The α_m values of Table 2 are independent of the parameter E/RT. Moreover, the

Table 2

m	α_m
2.5	0.124
3	0.197
4	0.279

Table 3

E/RT	α_1	E/RT	α_1
5	0.244	80	0.300
10	0.271	100	0.301
20	0.287	∞	0.305
50	0.297		

substitution of these data into Eq. (7) can be used to define the condition $d^2T/d\alpha^2 > 0$. This fact indicates that the T vs. α plots obtained from the new technique for $n > 2$ yield a minimum at the reacted fraction α_m. In contrast, it would be expected that the T–α plot shows inflection points where α_i values obey $d^2T/d\alpha^2 = 0$. Therefore, according to Eq. (7), α_i must fulfil the following condition:

$$\frac{2RT}{E}\left(\frac{1}{2\alpha_i} - \frac{n\ln(1-\alpha_i)+n-1}{n(1-\alpha_i)[-\ln(1-\alpha_i)]}\right)^2 + \frac{n\ln(1-\alpha_i)^2+(n-1)\ln(1-\alpha_i)+n-1}{n(1-\alpha_i)^2\ln(1-\alpha_i)^2} = \frac{1}{2\alpha_i^2} \quad (9)$$

The kinetic model with $n < 2$ leads to a solution of Eq. (9), and consequently to curves with an inflection point. Table 3 shows values of α_i for $n < 2$ ($n = 1.5$) as a function of E/RT. Finally, it must be pointed out that in the case of the kinetic law with $n = 2$, the α vs. T plot is convex, and hence neither maximum nor minimum nor inflection points have been found.

2.2. *Analysis of constant rate CRTA curves*

In this case the reaction rate is maintained at a constant value, C, throughout the process, and Eq. (1) becomes

$$C = An(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}\exp(-E/RT) \quad (10)$$

The same mathematical analysis as that carried out above led to the conclusion that the temperature vs. α plots obtained from CRTA data yield a minimum for all the n values of the Avrami–Erofeev kinetic models in Table 1. Solutions of $dT/d\alpha = 0$ were found for $n > 1$:

$$\alpha_m = 1 - \exp\left(\frac{1-n}{n}\right) \quad (11)$$

It can be seen from this that the values of the reacted fraction, α_m, at the minimum are independent of E/RT. These values are shown in Table 4.

In order to determine whether the above conclusion is valid, it was considered of interest to analyse the shape of a series of Avrami–Erofeev theoretical thermoanalytical curves calculated from Eqs. (4) and (10) by assuming a constant $C = 10^{-5}$ min^{-2} and the following kinetic parameters: $E = 120$ kJ mol^{-1} and $A = 10^9$ min^{-1}.

Table 4

n	α_m	n	α_m
1.5	0.283	3	0.487
2	0.393	4	0.528
2.5	0.451		

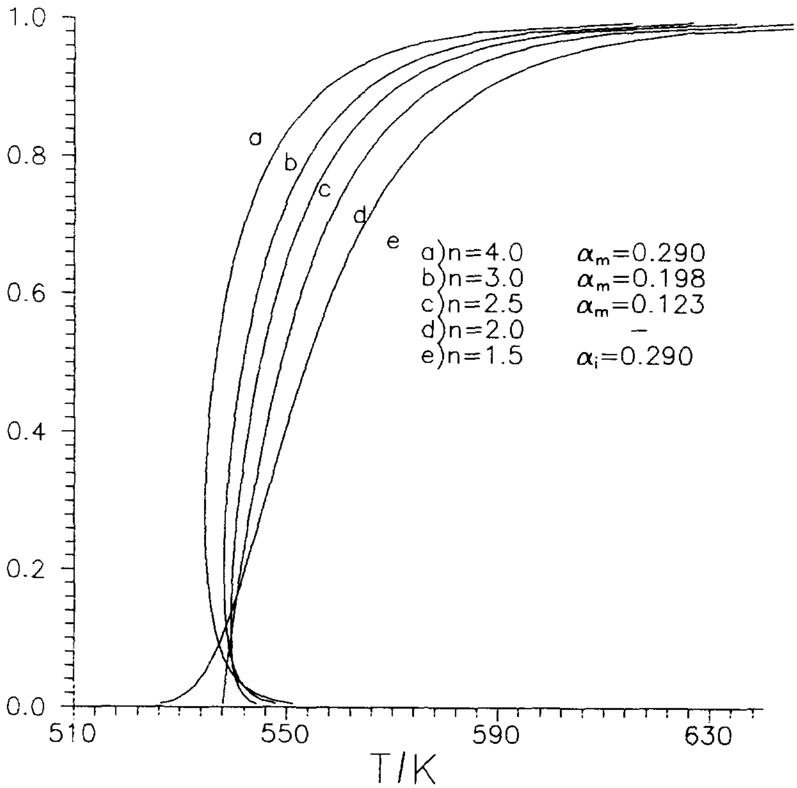

Fig. 1. Shape of a series of Avrami–Erofeev CRTA curves with constant acceleration of the transformation.

The new time-dependent CRTA curves (Eq. 4) are given in Fig. 1, and Fig. 2 shows the constant rate CRTA curves (Eq. 10).

It can be observed in Fig. 1 that the α vs. T plots only show an inflection point, at $\alpha = 0.290$, for $n < 2$ (A1.5). This result agrees with that prediction in Table 3 of $E/RT \approx 26$. However, the curve corresponding to $n = 2$ (A2) is convex and has neither a maximum nor a minimum nor an inflection point, according to the above statements. Finally, when $n > 2$ (A2.5, A3, A4) the $\alpha - T$ plots show that the reaction temperature decreases with increasing α until minimum values are reached at $\alpha_m = 0.277$ (A4), $\alpha_m = 0.198$ (A3) and $\alpha_m = 0.123$ (A2.5) according to Table 2.

In summary, we can see that these results are consistent with the predictions and that a mere glance at the shape of the time-dependent CRTA curves (Fig. 1) provides a rapid and easy way of discriminating between three groups of kinetic models fitting an Avrami–Erofeev equation: $n < 2$ (an inflection point), $n > 2$ (a minimum), $n = 2$ (neither maximum nor minimum nor inflection point, convex shape). In contrast, this trend would not be observed when constant rate CRTA is employed and it is not a possible to select unambiguously the correct mechanism,

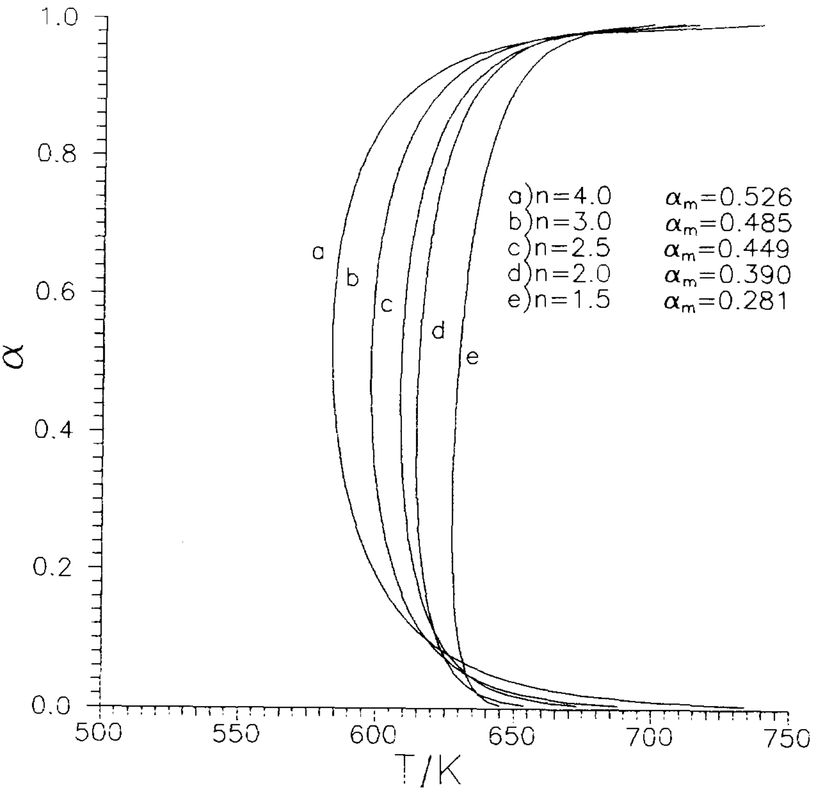

Fig. 2. Shape of Avrami–Erofeev CRTA curves at constant rate.

because from Fig. 2 we can see that all the Avrami–Erofeev kinetic models lead to curves with a minimum, α_m, whose values coincide with those calculated in Table 4. The differences between them are very small and the technique is not sensitive enough to allow discrimination.

The above results allow the conclusion that the availability of equipment for applying CRTA with constant acceleration of the transformation would permit a significant enhancement of the discrimination power of the kinetic models obeyed by solid state reactions from a single $\alpha - T$ curve. The development of an experimental tool for applying the described technique is now in progress in our laboratory.

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