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Shape analysis of the $\alpha - T$ curves obtained by CRTA with constant acceleration of the transformation

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Abstract

A novel aspect of CRTA is examined here, in which the heating of the sample is controlled in such a way that the reaction rate is increased as a linear function of time. It is demonstrated that this novel type of CRTA can discriminate, from a single curve, between the kinetic models which are described by the so-called "n-order" kinetic laws, which cannot be distinguished by constant transformation rate CRTA.

INTRODUCTION

It has been shown in previous papers [1–3] that the kinetic analysis of a single TG curve does not allow the discrimination of the actual kinetics of solid state reactions. Moreover, it has been pointed out that any theoretical TG curve calculated using a linear heating program by assuming a particular kinetic law also necessarily fits all other kinetic equations developed to describe solid state reactions, although the activation energy calculated is strongly dependent on the kinetic model assumed for performing the calculations.

A comparative study of the conventional thermogravimetric method (TG) and the controlled rate thermal analysis (CRTA) developed by Rouquerol [4] was reported in a previous paper [5]. It has been shown that this method allows a better discrimination between the kinetic models of solid state transformations than conventional TG. However, with the constant transformation rate with which most CRTA experiments have been carried out so far, one still finds the limitation that solid state reactions following n-order kinetics ($n \neq 0$) with an activation energy E_1 necessarily fit any kinetic law of n_1-order, giving an activation energy $E = (n/n_1)E_1$. This means that one constant rate CRTA curve does not supply enough informa-

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tion for calculating the parameter n when it differs from 0. The only possible way of providing the missing information is to carry out an extra experiment [6].

The aim of the present study is to propose the use of a specific heating program to discriminate the kinetic equation obeyed by the reaction from a single experiment. The new procedure, which has not been considered in the literature until now, involves the control of the reaction rate in such a way that it increases as a linear function of the time.

THEORETICAL

The reaction rate of a solid state reaction can be expressed as a function of the degree of conversion α at time t in the form

$$\frac{d\alpha}{dt} = Af(\alpha)\exp(-E/RT) \tag{1}$$

where A is the pre-exponential Arrhenius factor, E is the activation energy and $f(\alpha)$ a function depending on the kinetic model obeyed by the reaction.

The controlled rate thermal analysis with constant accceleration of the transformation proposed in this paper implies that the rate of reaction is increased as a linear function of time (instead of remaining constant, i.e. $d\alpha/dt = C$, as is normally the case)

$$\frac{d\alpha}{dt} = Ct \tag{2}$$

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

$$\frac{d\alpha}{dt} = (2C)^{1/2}\alpha^{1/2} \tag{3}$$

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

$$\frac{\alpha^{1/2}}{f(\alpha)} = \frac{A}{(2C)^{1/2}}\exp(-E/RT) \tag{4}$$

which can be rearranged after taking logarithms to give

$$\frac{1}{2}\ln\alpha - \ln f(\alpha) = \ln\frac{A}{(2C)^{1/2}} - \frac{E}{RT} \tag{5}$$

The plot of the left-hand-side of eqn. (5) as a function of the reciprocal of the temperature leads to a straight line, the slope of which yields the activation energy of the process provided that the proper $f(\alpha)$ function has been selected. The pre-exponential Arrhenius factor can be determined from the intercept.

ANALYSIS OF THE NEW CRTA CURVES

It has been shown in a previous paper [7] that the analysis of the shape of CRTA curves obtained at constant rate allows the mechanism of reactions obeying Avrami–Erofeev or diffusion kinetic laws to be discriminated. However, this method fails in discerning the kinetics of the so-called "n-order" reactions. It has been previously shown [8] that solid state reactions following n-order kinetics with an activation energy E_1 necessarily fit any kinetic equation of "n-order" giving an activation energy $E=(n/n_1)E_1$. Thus, it would be interesting to analyze the shape of the CRTA curves obtained with constant acceleration in order to determine if this method allows a better discrimination of the kinetic law obeyed by the reaction than CRTA with constant rate. To do this, it is necessary to determine the α values at which maximum, minimum or inflection points appear on the temperature versus α plots.

Equations (6) and (7) represent the first and second derivatives of T with respect to α, as obtained from eqn. (5)

$$\frac{dT}{d\alpha}=\frac{RT^2}{E}\left(\frac{1}{2\alpha}-\frac{f'(\alpha)}{f(\alpha)}\right) \tag{6}$$

$$\frac{d^2T}{d\alpha^2}=\frac{RT^2}{E}\left[\frac{2RT}{E}\left(\frac{1}{2\alpha}-\frac{f'(\alpha)}{f(\alpha)}\right)^2-\frac{1}{2\alpha^2}-\frac{f''(\alpha)f(\alpha)-f'(\alpha)^2}{f(\alpha)^2}\right] \tag{7}$$

The $f(\alpha)$, $f'(\alpha)$ and $f''(\alpha)$ functions corresponding to the kinetic models most commonly used in the literature are listed in Table 1.

The value of α at which there is a maximum or a minimum (α_m) is defined by setting $dT/d\alpha$ to 0. Thus from eqn. (6), we get

$$\frac{f'(\alpha_m)}{f(\alpha_m)}=\frac{1}{2\alpha} \tag{8}$$

The sign of eqn. (7) after substituting in the α_m calculated from eqn. (8) can be used as a criterion for discerning maxima or minima.

Solutions of eqn. (8) have been found only for nucleation and growth of nuclei (the Avrami–Erofeev equation) with $n>2$. The α_m values shown in Table 2 are independent of the parameter E/RT. Moreover, substitution of the data into eqn. (4) implies that $d^2T/d\alpha^2>0$, which indicates that the T versus α plots obtained from this new technique for solid state reactions following the Avrami–Erofeev kinetic law with $n>2$, yield a minimum at the reacted fraction α_m.

However, it would be expected that the $T-\alpha$ plots show inflection points, where the α_i values give $d^2T/d\alpha^2=0$. Therefore, according to eqn. (7), α_i must fulfil the condition

$$\frac{2RT}{E}\left(\frac{1}{2\alpha}-\frac{f'(\alpha)}{f(\alpha)}\right)^2-\frac{f''(\alpha)f(\alpha)-f'(\alpha)^2}{f(\alpha)^2}=\frac{1}{2\alpha^2} \tag{9}$$

TABLE 1

The $f(\alpha)$, $f'(\alpha)$ and $f''(\alpha)$ functions for the most common kinetic models used in the literature

Mech.	$f(\alpha)$	$f'(\alpha)$	$f''(\alpha)$
R_1	1	0	0
R_2	$(1-\alpha)^{1/2}$	$\frac{-1}{2(1-\alpha)^{1/2}}$	$\frac{-1}{4(1-\alpha)^{3/2}}$
R_3	$(1-\alpha)^{2/3}$	$\frac{-2}{3(1-\alpha)^{1/3}}$	$\frac{-2}{9(1-\alpha)^{4/3}}$
F_1	$(1-\alpha)$	-1	0
A_n	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	$\frac{n\ln(1-\alpha)+n-1}{[-\ln(1-\alpha)]^{1/n}}$	$\frac{-n+1+\frac{1-1/n}{\ln(1-\alpha)}}{(1-\alpha)[-\ln(1-\alpha)]^{1/n}}$
D_1	$\frac{1}{2\alpha}$	$\frac{-1}{2\alpha^2}$	$\frac{1}{\alpha^3}$
D_2	$\frac{-1}{\ln(1-\alpha)}$	$\frac{-1}{[\ln(1-\alpha)]^2(1-\alpha)}$	$\frac{-2-\ln(1-\alpha)}{(1-\alpha)^2[\ln(1-\alpha)]^3}$
D_3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$\frac{1/2-(1-\alpha)^{-1/3}}{[1-(1-\alpha)^{1/3}]^2}$	$\frac{3(1-\alpha)^{-1/3}-(1-\alpha)^{-2/3}-1}{3(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^3}$
D_4	$\frac{3}{2[(1-\alpha)^{-1/3}-1]}$	$\frac{-1}{2[(1-\alpha)^{1/3}-1]^2(1-\alpha)^{2/3}}$	$\frac{-2(1-\alpha)^{1/3}+1}{3[(1-\alpha)^{1/3}-1]^3(1-\alpha)^{5/3}}$

TABLE 2

Solutions of eqn. (8) for the Avrami–Erofeev equation with $n > 2$

	n	
	3	4
α_m	0.197	0.279

It has been found that the reactions following the kinetic laws R_2, R_3, F_1, D_2, D_3 and D_4 lead to a solution of eqn. (9) and, consequently, lead to curves with an inflection point. The expressions obtained for α_i are given in Table 3 together with the values calculated as a function of E/RT.

Finally, it must be pointed out that in the case of kinetic models D_1 and A_2, neither maxima, nor minima, nor inflection points have been found from the analysis of eqn. (9). However, these two kinetic models can easily be distinguished because the analysis of eqn. (6) indicates that the α versus T plot is convex in the case of the kinetic reaction fitting the A_2 kinetic model, and concave if the uni-dimensional kinetic law is involved.

TABLE 3

Expressions obtained for α_i and values of α_i calculated as a function of E/RT

Mechanism	Equation	E/RT	α_i
F_1	$(\alpha+1)^2=\frac{2}{1+(RT/E)}$	5	0.290
		10	0.348
		20	0.380
		50	0.400
		100	0.407
		∞	0.414
R_2	$\alpha=\frac{1-(RT/E)}{2}$	5	0.400
		10	0.450
		20	0.475
		50	0.490
		100	0.495
		∞	0.500
R_3	$(\alpha+3)^2=\frac{36}{3+(RT/E)}$	5	0.354
		10	0.408
		20	0.435
		50	0.453
		100	0.458
		∞	0.464
D_2	[a]	5	0.409
		10	0.574
		20	0.633
		50	0.663
		100	0.672
		∞	0.681
D_3	[a]	5	0.268
		10	0.431
		20	0.502
		50	0.542
		100	0.555
		∞	0.568
D_4	[a]	5	0.345
		10	0.509
		20	0.576
		50	0.607
		100	0.618
		∞	0.628

[a] A closed form for α_i was not found; α_i as a factor of E/RT was determined from numerical solution of eqn. (9).

It must be pointed out that the time-dependent CRTA outlined here permits a rapid discrimination of the Avrami–Erofeev kinetic models A_2 and A_3, just from an inspection of the shape of the $\alpha-T$ plot, without requiring previous calculations. This is not true for CRTA at constant rate.

RESULTS

In order to check the above conclusions, it was considered of interest to analyze the shape of a series of theoretical curves calculated from eqn. (4) by assuming all the kinetic models included in Table 1. The curves given in Figs. 1–3 were calculated by assuming a value of $C = 10^{-5}\ \text{min}^{-2}$ and the kinetic parameters $E = 120\ \text{kJ mol}^{-1}$ and $A = 10^{-9}\ \text{min}^{-1}$.

It can be observed that in the case of the kinetic model A_3 (Fig. 2), the reaction temperature decreases with increasing α until a minimum value is reached at $\alpha_m = 0.197$, while the $\alpha-T$ plot corresponding to the A_2 model is convex according to the results included in Table 3. Moreover, it can be seen that the curves calculated in Figs. 3 and 1 for the diffusion kinetic models D_2 and D_3, and for the n-order kinetic equations R_2, R_3 and F_1 respectively, present an inflection point at values of α_i that agree with those predicted in Table 3.

In order to confirm the viability of time-dependent CRTA for discriminating among the different kinetic models, kinetic analyses of the $\alpha-T$ curves simulated by assuming the kinetic models R_3, A_2 and D_4 (see Figs.

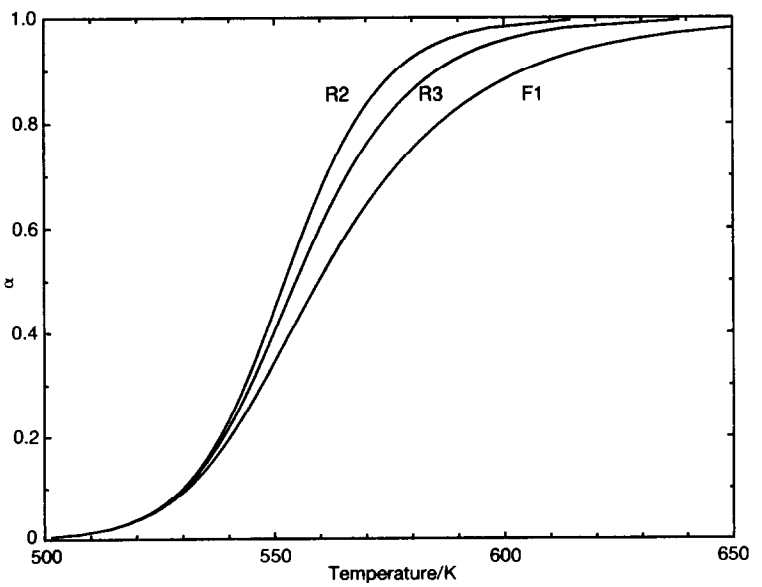

Fig. 1. $\alpha-T$ plot corresponding to the "n-order" kinetic models calculated by assuming a value of $C = 10^{-5}\ \text{min}^{-2}$ and the kinetic parameters $E = 120\ \text{kJ mol}^{-1}$ and $A = 10^{-9}\ \text{min}^{-1}$.

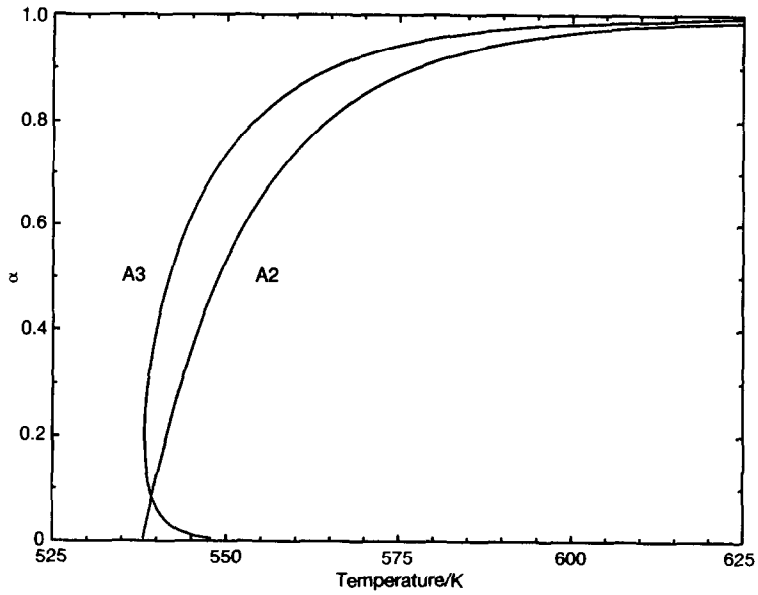

Fig. 2. $\alpha-T$ plot corresponding to the Avrami–Erofeev kinetic models calculated by assuming a value of $C = 10^{-5}\,\mathrm{min}^{-2}$ and the kinetic parameters $E = 120\,\mathrm{kJ\,mol}^{-1}$ and $A = 10^{-9}\,\mathrm{min}^{-1}$.

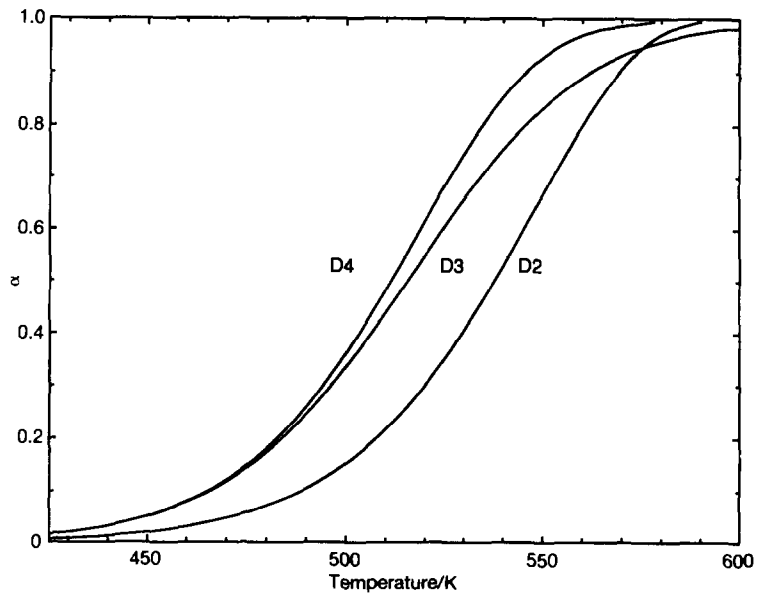

Fig. 3. $\alpha-T$ plot corresponding to the diffusion kinetic models calculated by assuming a value of $C = 10^{-5}\,\mathrm{min}^{-2}$ and the kinetic parameters $E = 120\,\mathrm{kJ\,mol}^{-1}$ and $A = 10^{-9}\,\mathrm{min}^{-1}$.

1, 2 and 3, respectively) were performed. Tables 4–6 show the values of E and A determined from these plots by means of eqn. (5) after considering the $f(\alpha)$ functions corresponding to the different kinetic models listed in Table 1.

TABLE 4

Kinetic parameters calculated from data of Fig. 1 (R_3) by means of eqn. (5)

Mechanism	E/kJ mol^{-1}	log A	r
R_2	103.0 ± 0.7	6.44 ± 0.14	0.9980
R_3	120.0 ± 0.1	8.11 ± 0.03	1.0000
F_1	154.1 ± 1.3	11.46 ± 0.29	0.9962
A_2	82.8 ± 3.5	4.59 ± 0.76	0.9232
A_3	59.1 ± 4.2	2.22 ± 0.91	0.8179
D_2	194.4 ± 7.0	14.56 ± 1.51	0.9425
D_3	247.0 ± 4.8	19.07 ± 1.05	0.9817
D_4	212.9 ± 6.2	15.73 ± 1.34	0.9611

TABLE 5

Kinetic parameters calculated from data of Fig. 2 (A_2) by means of eqn. (5)

Mechanism	E/kJ mol^{-1}	log A	r
R_2	123.8 ± 6.2	8.42 ± 1.34	0.8965
R_3	148.2 ± 6.2	10.80 ± 1.35	0.9232
F_1	197.1 ± 6.3	15.45 ± 1.38	0.9529
A_2	120.0 ± 0.2	8.11 ± 0.04	1.0000
A_3	94.3 ± 2.1	5.56 ± 0.46	0.9763
D_2	204.6 ± 18.7	15.57 ± 4.06	0.7414
D_3	280.4 ± 18.8	22.28 ± 4.09	0.8331
D_4	231.5 ± 18.7	17.53 ± 4.06	0.7811

TABLE 6

Kinetic parameters calculated from data of Fig. 3 (D_4) by means of eqn. (5)

Mechanism	E/kJ mol^{-1}	log A	r
R_2	54.6 ± 1.2	2.40 ± 0.29	0.9768
R_3	62.5 ± 1.8	3.28 ± 0.43	0.9610
F_1	78.2 ± 3.0	5.05 ± 0.72	0.9337
A_2	37.9 ± 3.1	0.72 ± 0.73	0.7809
A_3	24.5 ± 3.1	−0.80 ± 0.73	0.6270
D_2	111.5 ± 0.7	7.81 ± 0.17	0.9980
D_3	135.7 ± 1.2	9.88 ± 0.29	0.9960
D_4	120.0 ± 0.2	8.11 ± 0.04	0.9999

Those results indicate that the analysis from eqn. (5) of the $\alpha-T$ traces obtained under a controlled linear increase of the reaction rate, together with an inspection of the curve shape, can discriminate between the different kinetic laws, with the apparent exception of "n-order" reactions. The results in Table 4 show that very good regression coefficients are obtained by assuming the F_1 or R_2 reaction models in the kinetic analysis from eqn. (5) of the $\alpha-T$ plots constructed in Fig. 1 by considering an R_3 kinetic law. Moreover, the values of α_i shown in Table 3 are too close to help the discrimination. Thus, it is interesting to propose an alternative procedure for performing the kinetic analysis of "n-order" reactions. In this case, eqn. (5) can be rearranged in the form

$$\frac{1}{2}\ln\alpha = \ln\frac{A}{(2C)^{1/2}} - \frac{E}{RT} + n\ln(1-\alpha) \tag{10}$$

If we derive eqn. (10) with respect to $\mathrm{d}\ln(1-\alpha)$ following the method proposed by Freeman and Carroll [9] for analysis of conventional DTG curves, we get

$$\frac{1}{2}\frac{\mathrm{d}\ln\alpha}{\mathrm{d}\ln(1-\alpha)} = -\frac{E}{R}\frac{\mathrm{d}(1/T)}{\mathrm{d}\ln(1-\alpha)} + n \tag{11}$$

or

$$\frac{1}{2}\frac{\Delta\ln\alpha}{\Delta\ln(1-\alpha)} = -\frac{E}{R}\frac{\Delta(1/T)}{\Delta\ln(1-\alpha)} + n \tag{12}$$

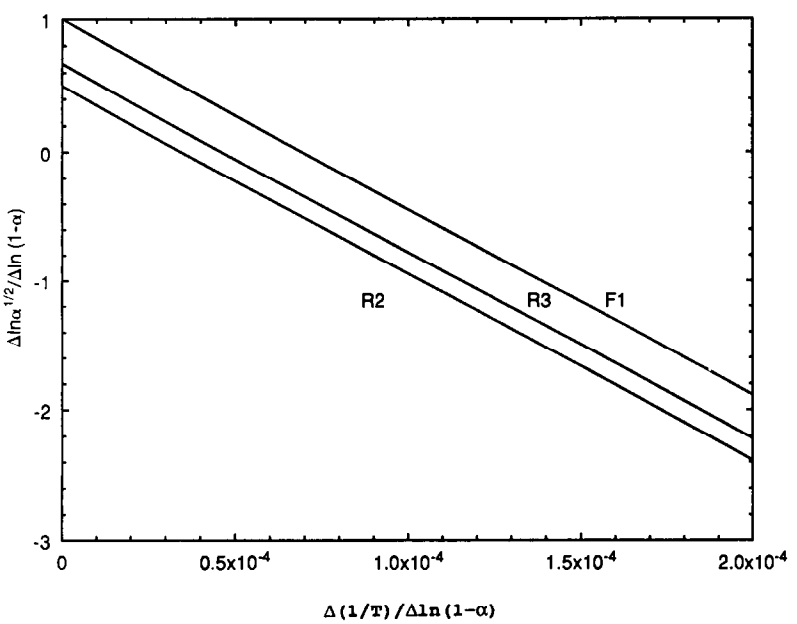

Fig. 4. The corresponding plots of $\Delta\ln\alpha^{1/2}/\Delta\ln(1-\alpha)$ as a function of $\Delta(1/T)/\Delta\ln(1-\alpha)$ for the "n-order" kinetic models R_2, R_3 and F_1.

TABLE 7

Values of the activation energies and the reaction orders obtained from Fig. 1

Mechanism	E/kJ mol^{-1}	n	r
F_1	120	1	1.0000
R_2	120	1/2	1.0000
R_3	120	2/3	1.0000

The plot of eqn. (11) or (12) against $d(1/T)/d\ln(1-\alpha)$ or $\Delta(1/T)/\Delta\ln(1-\alpha)$ yields a straight line with slope $-E/RT$ and an intercept equal to n. Thus this method allows one to determinate simultaneously both E and the "reaction order" n without a previous knowledge of this parameter.

In order to test the validity of the above conclusions, we have carried out the kinetic analysis of the "n-order" curves R_2, R_3 and F_1 shown in Fig. 1 by means of eqn. (12). The corresponding plots of $\Delta\ln\alpha^{1/2}/\Delta\ln(1-\alpha)$ as a function of $\Delta(1/T)/\Delta\ln(1-\alpha)$ are shown in Fig. 4. The values of the activation energies and the reaction order calculated from these plots are given in Table 7.

The results obtained demonstrate that, in contrast to CRTA with constant rate, CRTA with constant acceleration, as proposed here, allows a good discrimination of "n-order" reactions.

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