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CORRELATION BETWEEN THE SHAPE OF CONTROLLED-RATE THERMAL ANALYSIS CURVES AND THE KINETICS OF SOLID-STATE REACTIONS

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ABSTRACT

A method for determining the real kinetics of solid-state reactions from analysis of the shape of controlled-rate thermal analysis curves is proposed. It is shown that this procedure provides an easy way for discriminating between "*n*-order", Avrami–Erofeev and diffusion kinetic laws. The theoretical conclusions were checked experimentally by studying the thermal decomposition of anhydrous nickel nitrate.

INTRODUCTION

The conventional non-isothermal methods of kinetic analysis of solid-state reactions are very popular. In general, it seems to be accepted that these methods permit the proper determination of the kinetic parameters of a reaction, although opinions differ [1,2] regarding their usefulness for determining the kinetic model obeyed by the reaction.

It has been proved previously [3–5] that the actual kinetics of solid-state reactions cannot be discerned by means of the kinetic analysis of a single thermogravimetric (TG) curve. Moreover, it has been pointed out that any theoretical TG curve calculated using a linear heating programme by assuming a particular kinetic law does not necessarily fit all the kinetic equations developed for describing solid-state reactions, although the activation energy obtained is strongly dependent on the kinetic law assumed in performing the calculations. By way of an example, Fig. 1 shows that a unique TG curve can be calculated by assuming three different kinetic models: a diffusion law (D3), an Avrami–Erofeev equation (A2) and a random nucleation unimolecular decay law (F1).

In an earlier work [6] a comparative study of the conventional TG method and the constant-rate thermal analysis (CRTA) technique developed by Rouquerol [7] was carried out. It was demonstrated that the CRTA method allows the reaction mechanism to be discerned with the only exception being "*n*-order" kinetic laws.

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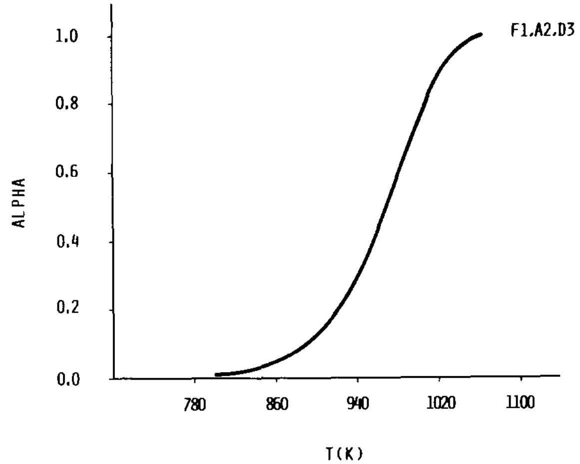

Fig. 1. A single TG curve for three different kinetic models. F1: $E=167$ kJ mol^{-1}, $A=1.6\times10^6$ s^{-1}. A2: $E=76$ kJ mol^{-1}, $A=0.12\times10^2$ s^{-1}. D3: $E=308$ kJ mol^{-1}, $A=6\times10^{12}$ s^{-1}.

The aim of the present study was to propose a new method for determining the kinetics of solid-state reactions from the analysis of the shape of CRTA curves.

EXPERIMENTAL

$Ni(NO_3)_2 \cdot 6H_2O$ Panreac AnalaR was used. The anhydrous salt was prepared by dehydrating the corresponding hexahydrate in situ at 150 °C.

The experiments were performed in a Cahn RG electrobalance model 2000. The apparatus was modified in order to monitor the furnace temperature in such a way that the total decomposition rate remains constant over the entire decomposition range. This was attained both by controlling the residual pressure in the close vicinity of the sample and by maintaining a constant value of the pumping rate which can be selected by means of a valve. It is worth pointing out that the thermobalance was modified without losing the original performance specified by the supplier.

The CRTA curves for nickel nitrate were recorded using a residual pressure of 10^{-4} Torr and a decomposition rate of 2.5×10^{-3} min^{-1}. The sample size was 25 mg.

ANALYSIS OF THE SHAPE OF CRTA CURVES

It is well known that the rate of a solid-state reaction is given by the general expression

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

If the thermoanalytical curve is obtained at a constant decomposition rate ($C = \mathrm{d}\alpha/\mathrm{d}t$), then according to the CRTA method eqn. (1) can be rearranged, after taking logarithms, in the form

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

The plot of the left-hand side of eqn. (2) 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.

It has been shown previously [8,9] that the analysis of the shape of conventional DTA or DTG curves provides valuable information for elucidating the actual kinetic law obeyed by a reaction. However, no similar analysis of thermoanalytical traces obtained from CRTA experiments has been described. Therefore, it was considered of interest to determine the α values at which maxima, minima or inflexion points appear on the temperature versus α (or time) plots calculated by assuming the $f(\alpha)$ functions most commonly used in the literature for describing solid-state reactions.

Equations (3) and (4) represent the first and second derivatives of T with respect to α, as obtained from eqn. (2)

$$\frac{\mathrm{d}T}{\mathrm{d}\alpha} = -\frac{RT^2}{E}\frac{f'(\alpha)}{f(\alpha)} \tag{3}$$

$$\frac{\mathrm{d}^2T}{\mathrm{d}\alpha^2} = \frac{RT^2}{E}\left[\frac{2RT}{E}\left(\frac{f'(\alpha)}{f(\alpha)}\right)^2 - \frac{f''(\alpha)f(\alpha) - f'(\alpha)^2}{f(\alpha)^2}\right] \tag{4}$$

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.

A plot of T as a function of α can show a maximum or a minimum at the α_m value at which $\mathrm{d}T/\mathrm{d}\alpha = 0$, i.e

$$f'(\alpha_\mathrm{m}) = 0 \tag{5}$$

The sign of eqn. (4), after substituting in the α_m calculated from eqn. (5), can be used as a criterion for discerning maxima or minima.

Solutions of eqn. (5) have been found only for Avrami–Erofeev kinetic models with $n > 1$.

$$\alpha_\mathrm{m} = 1 - \exp\left(\frac{1-n}{n}\right) \tag{6}$$

This equation points out that α_m values (shown in Table 2) are independent of E/RT. Moreover, the substitution of these data into eqn. (4) points out that $\mathrm{d}^2T/\mathrm{d}\alpha^2 > 0$. This fact indicates that the T versus α plots obtained from CRTA techniques for solid-state reactions following Avrami–Erofeev mechanisms yield a minimum at the reacted fraction α_m.

TABLE 1

Algebraic expressions for the $f(\alpha)$, $f'(\alpha)$ and $f''(\alpha)$ functions for the most common mechanism operating in solid-state reactions

Mechanism	Symbol	$f(\alpha)$	$f'(\alpha)$	$f''(\alpha)$
Zero-order mechanism	R1	1	0	0
Phase boundary controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$	$\frac{-1}{2(1-\alpha)^{1/2}}$	$\frac{-1}{4(1-\alpha)^{3/2}}$
Phase boundary controlled reaction (contracting volume)	R3	$(1-\alpha)^{2/3}$	$\frac{-2}{3(1-\alpha)^{1/3}}$	$\frac{-2}{9(1-\alpha)^{4/3}}$
Unimolecular decay law	F1	$(1-\alpha)$	-1	0
Random nucleation and growth of nuclei (Avrami–Erofeev equation)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	$\frac{n\ln(1-\alpha)+n-1}{[-\ln(1-\alpha)]^{1/n}}$	$\frac{-n+1+\frac{1-1/n}{\ln(1-\alpha)}}{(1-\alpha)[-\ln(1-\alpha)]^{1/n}}$
One-dimensional diffusion (parabolic law)	D1	$1/2\alpha$	$\frac{-1}{2\alpha^2}$	$\frac{1}{\alpha^3}$
Two-dimensional diffusion	D2	$1/[-\ln(1-\alpha)]$	$\frac{-1}{[\ln(1-\alpha)]^2[1-\alpha]}$	$\frac{-2-\ln(1-\alpha)}{(1-\alpha)^2[\ln(1-\alpha)]^3}$
Three-dimensional diffusion (Jander equation)	D3	$\frac{3(1-\alpha)^{2/3}}{2\left[1-(1-\alpha)^{1/3}\right]}$	$\frac{1/2-(1-\alpha)^{-1/3}}{\left[1-(1-\alpha)^{1/3}\right]^2}$	$\frac{3(1-\alpha)^{-1/3}-(1-\alpha)^{-2/3}-1}{3(1-\alpha)^{2/3}\left[1-(1-\alpha)^{1/3}\right]^3}$
Three-dimensional diffusion (Ginstein–Brounshtein equation)	D4	$\frac{3}{2\left[(1-\alpha)^{-1/3}-1\right]}$	$\frac{-(1-\alpha)^{-4/3}}{2\left[(1-\alpha)^{-1/3}-1\right]^2}$	$\frac{2\left[(1-\alpha)^{1/3}-1\right]+1}{3(1-\alpha)^{8/3}\left[(1-\alpha)^{-1/3}-1\right]^3}$

TABLE 2

Calculated values for α_m according to eqn. (6) for Avrami–Erofeev kinetic models with $n > 1$

n	2.0	3.0	4.0
α_m	0.393	0.487	0.528

On the other hand, it would be expected that the T versus α plots show inflection points where α_i values give $d^2T/d\alpha^2 = 0$. Therefore, according to eqn. (4) α_i must fulfill the following condition

$$[f'(\alpha_i)]\left[\frac{2}{E/RT} + 1\right] - f(\alpha_i)f''(\alpha_i) = 0 \tag{7}$$

It has been found that only diffusion-controlled reactions obeying the kinetic laws D2, D3 and D4 lead to a solution of eqn. (7). 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 both "n-order" reaction (R2, R3 and F1) and reactions fitting the unidimensional diffusion law (D1) neither maxima nor minima nor inflection points have been found from the analysis of eqns. (5) and (7). However, it is noteworthy that these two groups of kinetic models can be easily distinguished. In fact, analysis of eqn. (3)

TABLE 3

Mathematical expressions obtained for α_i according to eqn. (7) and the calculated values as a function of E/RT

Mechanism	Equation	E/RT	α_i
D2	$\alpha_i = 1 - e^{(2RT/E)-1}$	10	0.551
		20	0.593
		50	0.617
		100	0.625
		∞	0.632
D3	$\alpha_i = 1 - \left[\frac{8(RT/E)+6}{4(RT/E)+5+\sqrt{4(RT/E)+7}}\right]^3$	10	0.413
		20	0.465
		50	0.496
		100	0.506
		∞	0.517
D4	$\alpha_i = 1 - \left(\frac{RT}{2E} + \frac{3}{4}\right)^3$	10	0.488
		20	0.534
		50	0.561
		100	0.570
		∞	0.578

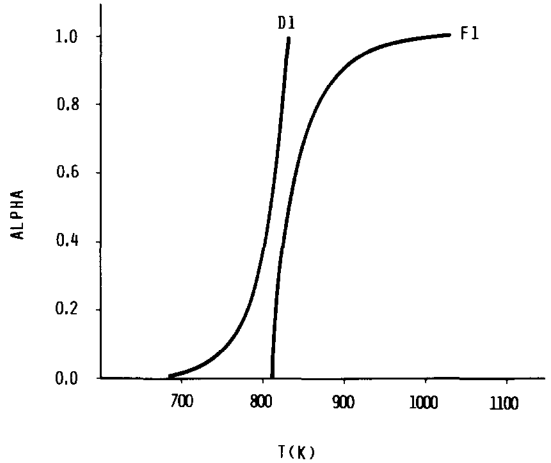

Fig. 2. Shape of the theoretical CRTA curves corresponding to D1 (concave) and F1 (convex) kinetic models obtained assuming $E = 167$ kJ mol^{-1}, $A = 17 \times 10^5$ s^{-1} and $C = 3 \times 10^{-4}$ s^{-1}.

indicates that the plot of the reacted fraction, α, as a function of temperature is convex in the case of "n-order" reactions and concave if the unidimensional diffusion law is involved.

In order to determine whether the above conclusion works it was considered of interest to analyse the shape of a series of theoretical thermoanalytical curves calculated from eqn. (2) by assuming a constant reaction rate $C = d\alpha/dt = 0.0003$ s^{-1}. The CRTA curves given in Figs. 2 to 5 were calculated assuming all the kinetic models quoted in Table 1 and the following kinetic parameters: $E = 167$ kJ mol^{-1}, $A = 1.7 \times 10^5$ s^{-1}.

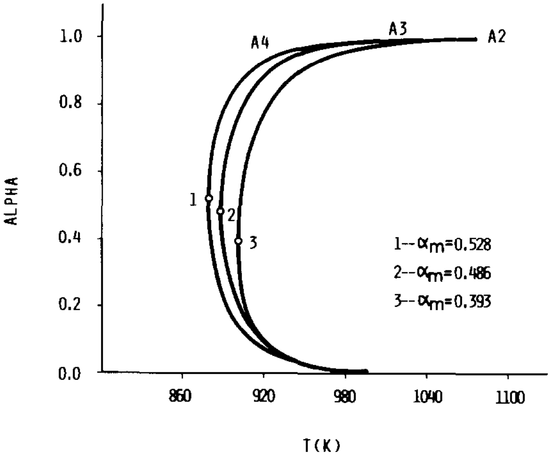

Fig. 3. Shape of the theoretical CRTA curves corresponding to the A2, A3 and A4 kinetic models obtained assuming the same kinetic parameters as in Fig. 2.

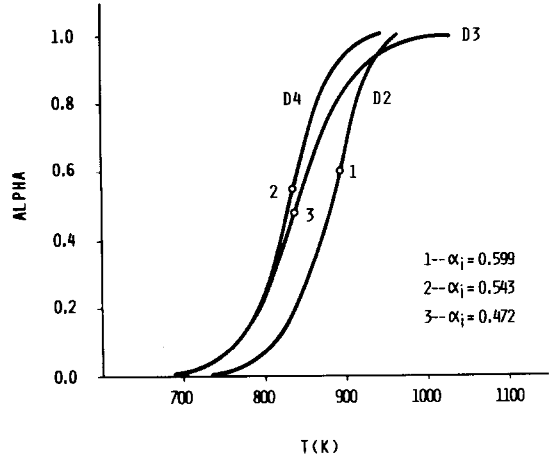

Fig. 4. Shape of the theoretical CRTA curves corresponding to the D2, D3 and D4 kinetic models obtained assuming the same kinetic parameters as in Fig. 2.

It can be observed that the curves calculated for the D1 and F1 laws in Fig. 2 are concave and convex, respectively, according to the above conclusions. On the other hand the α versus T plots corresponding to the Avrami–Erofeev kinetic models, A2, A3 and A4 shows in Fig. 3, show that the reaction temperature decreases with increasing α until a minimum value is reached at $\alpha_m = 0.393$, 0.486 and 0.528, respectively, according to the results included in Table 2. Moreover, the α_i value shown in Fig. 4 for the CRTA curves calculated for the diffusion models D2, D3 and D4 agree with those forecast in Table 3 for $E/RT \approx 25$. Finally, Figs. 2 and 5 show that "n-order" reactions, R2, R3 and F1, do not have maxima, minima, or

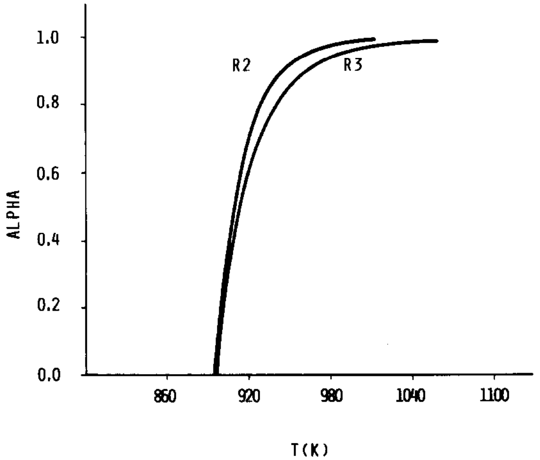

Fig. 5. Shape of the theoretical CRTA curves corresponding to the R2 and R3 kinetic models obtained assuming the same kinetic parameters as in Fig. 2.

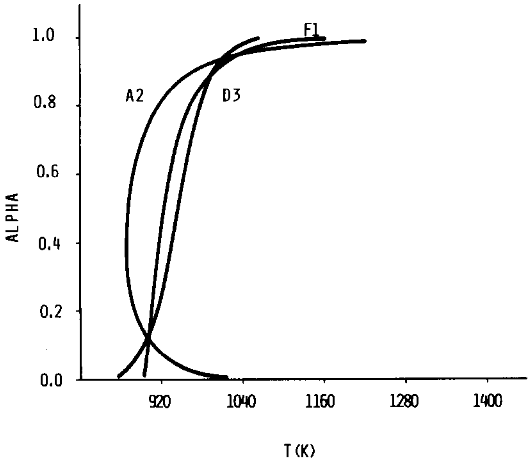

Fig. 6. Discrimination between the three kinetic models of Fig. 1 by means of the CRTA method. $C = 3 \times 10^{-4}$ s^{-1}.

inflexion points. Similar results would be obtained if the thermoanalytical curves were calculated using other kinetic parameters.

On the other hand it is noteworthy that the CRTA curves determined in Fig. 6 for the F1, A2 and D3 models are clearly discriminated despite the fact that the corresponding TG curves calculated from the same kinetic parameters overlap (as shown in Fig. 1).

To summarize, it can be concluded that a mere glance at the shape of the CRTA curves provides an easy way of discriminating between "*n*-order", Avrami–Erofeev and diffusion kinetic models; in particular, the shape of the Avrami–Erofeev model is very characteristic. However, the differences in behaviour of similar models within a family are small and it would be difficult to select unambiguously the correct mechanism.

Moreover, the data included in Figs. 1 and 6 show that a comparison of the kinetic parameters calculated from the kinetic analysis of both a CRTA curve and a conventional TG curve obtained with a linear heating program for a particular solid-state reaction would supply a good method for properly determining the reaction mechanism.

RESULTS

In order to check the above conclusion experimentally the CRTA curve was obtained for the thermal decomposition of anhydrous nickel nitrate (Fig. 7). It has been shown previously [10] that this transformation obeys the Avrami–Erofeev kinetic law with an exponent of $n = 2$. This result has been interpreted by a reaction mechanism that involves instantaneous nucleation on the surface of the crystal with subsequent growth of the nuclei into

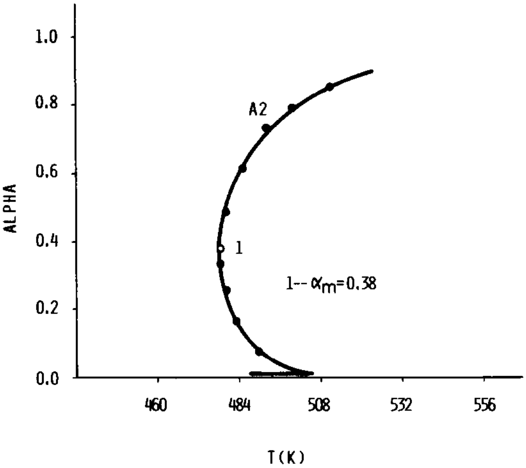

Fig. 7. Experimental CRTA curve for the thermal decomposition of anhydrous nickel nitrate. $C = 2.5 \times 10^{-3}$ min^{-1}.

particles. The shape of the α versus T plot shown in Fig. 7 is very characteristic of an Avrami–Erofeev model and the curve has a minimum on the T axis at $\alpha = 0.38$. This value agrees very well with that forecast in Table 2 for $n = 2$.

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APPENDIX: NOMENCLATURE

α	Reacted fraction
t	Time
T	Absolute temperature
R	Gas constant
E	Activation energy
A	Pre-exponential Arrhenius factor
n	Exponent of the Avrami–Erofeev kinetic models