

SIMULTANEOUS DETERMINATION OF THE ACTIVATION ENERGY AND THE REACTION KINETIC MODEL FROM THE ANALYSIS OF A SINGLE CURVE OBTAINED BY A NOVEL METHOD

**CRTA with constant acceleration of the
transformation**

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Abstract

It has been demonstrated that a single plot of the values of $\Delta \ln \alpha^{1/2} / \Delta \ln(1 - \alpha)$ (taken from a single $\alpha - T$ curve obtained under a controlled linear increase of the reaction rate) as a function of the corresponding values of $\Delta(1/T) / \Delta \ln(1 - \alpha)$ permits the simultaneous determination of both the activation energy and the kinetic model in accordance with a solid state reaction.

Keywords: CRTA, activation energy, kinetics, reaction kinetic model

Introduction

It has been proposed in a previous paper the novel method of Controlled Rate Thermal Analysis with Constant Acceleration of the Transformation that implies to control the temperature of the sample in such a way that the reaction rate is linear function of the time (i.e.; $d\alpha/dt = Ct$, C being a constant arbitrarily selected by the user) in contrast to the method formerly introduced by Rouquerol [1] and Paulik [2] that implies to maintain the reaction rate at a strictly constant value all over the process. It has been claimed [3] that the analysis of a single time dependent-CRTA curve allows to discriminate among the different kinetic models proposed in literature to describe solid state reactions, including "n order" reactions that cannot be discerned from the more conventional CRTA method. The scope of the present paper is to propose a new method of kinetic analysis that allows the simultaneous determination of the ac-

tivation energy and the kinetic model according to the reaction from a single linear plot of data taken from a single α - T curve obtained under a linear increase of the reaction rate.

Theoretical

The reaction rate of a solid state reaction, $d\alpha/dt$, can be expressed as a function of the reacted fraction, α , as:

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

where A is the preexponential factor of Arrhenius, $f(\alpha)$ is a function depending on the kinetic model and E is the activation energy.

The controlled Rate Thermal Analysis with constant acceleration of the transformation proposed in this paper implies that the rate of reaction is increased as a linear function of the time instead of remaining constant (i.e. $d\alpha/dt = C$) like it is most often done.

$$\frac{d\alpha}{dt} = Ct \quad (2)$$

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

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

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

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

If we differentiate the logarithmic form of Eq. (4) with respect to $d \ln(1 - \alpha)$, following the treatment applied by Freeman and Carrol [4] and Criado, Dollimore and Heal [5] to the kinetic equation describing conventional TG plots, we get

$$\frac{d \ln \alpha^{1/2}}{d \ln(1 - \alpha)} = -\frac{E}{R} \frac{d(1/T)}{d \ln(1 - \alpha)} + \frac{d \ln f(\alpha)}{d \ln(1 - \alpha)} \quad (5)$$

that would be also written in the form

$$\frac{\Delta \ln \alpha^{1/2}}{\Delta \ln(1 - \alpha)} = -\frac{E}{R} \frac{\Delta(1/T)}{\Delta \ln(1 - \alpha)} + \frac{\Delta \ln f(\alpha)}{\Delta \ln(1 - \alpha)} \tag{6}$$

Analysis of phase boundary controlled reactions ("n order" reactions)

If the reaction is in accordance with "n order" kinetic law then $f(\alpha) = (1 - \alpha)^n$ and Eqs (5) and (6) becomes, respectively,

$$\frac{d \ln \alpha^{1/2}}{d \ln(1 - \alpha)} = -\frac{E}{R} \frac{d(1/T)}{d \ln(1 - \alpha)} + n \tag{7}$$

and

$$\frac{\Delta \ln \alpha^{1/2}}{\Delta \ln(1 - \alpha)} = -\frac{E}{R} \frac{\Delta(1/T)}{\Delta \ln(1 - \alpha)} + n \tag{8}$$

The plot of the left hand side of Eqs (7) or (8) vs. $d(1/T)/d \ln(1 - \alpha)$ or $\Delta(1/T)/\Delta \ln(1 - \alpha)$, respectively, should be a straight line with a slope $-E/R$ and

Table 1 Algebraic expression for $f(\alpha)$ and $d \ln f(\alpha)/d \ln(1 - \alpha)$ for the most common mechanism operating in solid-state reactions

Mechanism (symbol)*	$f(\alpha)$	$\frac{d \ln f(\alpha)}{d \ln(1 - \alpha)}$
Zero-order mechanism (R_1)	1	0
Phase boundary controlled reaction (contracting area) (R_2)	$(1 - \alpha)^{1/2}$	1/2
Phase boundary controlled reaction (contracting volume) (R_3)	$(1 - \alpha)^{2/3}$	2/3
Unimolecular decay law (F_1)	$(1 - \alpha)$	1
Avrami-Erofeev (A_m)	$m(1 - \alpha)[- \ln(1 - \alpha)]^{1 - 1/m} \left(1 - \frac{1}{n}\right) \frac{1}{\ln(1 - \alpha)} + 1$	
Unidimensional diffusion (D_1)	$\frac{1}{2\alpha}$	$\frac{1 - \alpha}{\alpha}$
Two-dimensional diffusion (D_2)	$\frac{-1}{\ln(1 - \alpha)}$	$-\frac{1}{\ln(1 - \alpha)}$
Three-dimensional diffusion (Jander mechanism) (D_3)	$\frac{3(1 - \alpha)^{2/3}}{2[1 - (1 - \alpha)^{1/3}]}$	$\frac{(1 - \alpha)^{1/3} - 2}{3[(1 - \alpha)^{1/3} - 1]}$
Three-dimensional diffusion (Ginsting-Brounshtein mechanism) (D_4)	$\frac{3}{2[(1 - \alpha)^{-1/3} - 1]}$	$\frac{-1}{3[(1 - \alpha)^{1/3} - 1]}$

*Symbols of Sharp *et al.* [7] have been used.

an intercept equal to n . Therefore, this method allows one to determine simultaneously both the activation energy and the reaction order without a previous knowledge of this last parameter. It must be pointed out that using the CRTA method at strictly constant reaction rate is possible neither discriminating the value of n nor determining the actual value of the activation energy as shown in previous papers [6].

Analysis of both diffusion controlled reaction and reactions controlled by random nucleation and growth of nuclei (Avrami-Erofeev kinetic)

If the following relationship can be established

$$\frac{d \ln f(\alpha)}{d \ln(1 - \alpha)} = a \frac{d \ln \alpha^{1/2}}{d \ln(1 - \alpha)} + b \quad (9)$$

(a and b being constants), from Eqs (5) and (9) one obtains

$$\frac{d \ln \alpha^{1/2}}{d \ln(1 - \alpha)} = - \frac{cE}{R} \frac{d(1/T)}{d \ln(1 - \alpha)} + d \quad (10)$$

that would be also written in the form

$$\frac{\Delta \ln \alpha^{1/2}}{\Delta \ln(1 - \alpha)} = - \frac{cE}{R} \frac{\Delta (1/T)}{\Delta \ln(1 - \alpha)} + d \quad (11)$$

where $c = 1/(1-a)$ and $d = b/(1-a)$.

By comparing Eqs (7) and (10) it can be seen that, if Eq. (9) applies, then the reaction would be seen to obey an " n order" kinetic law. In this case an ap-

Table 2 Values of a and b calculated from Eq. (9) together with their linear correlation coefficients, and the values determined for the Eq. (10)

Kinetic equation	a	b	r	$c = E'/E$	d
F_1	-	-	-	1	1
D_1	-	-	-	1	0
R_2	-	-	-	1	1/2
R_3	-	-	-	1	1/3
A_2	1.00	0.79	1	∞	∞
A_3	1.34	0.72	1	-2.92	-2.11
D_1	-2.00	0.00	1	0.33	0.00
D_2	-2.00	0.42	1	0.33	0.14
D_3	-2.00	0.93	1	0.33	0.31
D_4	-2.00	0.59	1	0.33	0.20

parent reaction order $n = d$ and an apparent activation energy $E' = cE$ would be obtained.

In order to check if the above assumptions work in the case of reactions controlled by diffusion or Avrami-Erofeev kinetic laws we have collected in Table 1 the corresponding mathematical expressions of the function $f(\alpha)$ and $d \ln f(\alpha) / d \ln(1 - \alpha)$. The values of the constants a and b calculated from Eq. (9) together with their linear correlation coefficients and the values determined for the constant c and d of Eq. (10) are shown in Table 2. The values that would be obtained for " n order" reactions have been included as well for a comparison.

The above results allow to conclude that, for a given time-dependent CRTA curve, the plot of the values of $d \ln \alpha^{1/2} / d \ln(1 - \alpha)$ (or $\Delta \ln \alpha^{1/2} / \Delta \ln(1 - \alpha)$) as a function of $d(1/T) / d \ln(1 - \alpha)$ (or $\Delta(1/T) / \Delta \ln(1 - \alpha)$) leads to a straight line whose intercept is characteristic of the kinetic model according to the reaction. Moreover, once the kinetic model has been established, the real activation en-

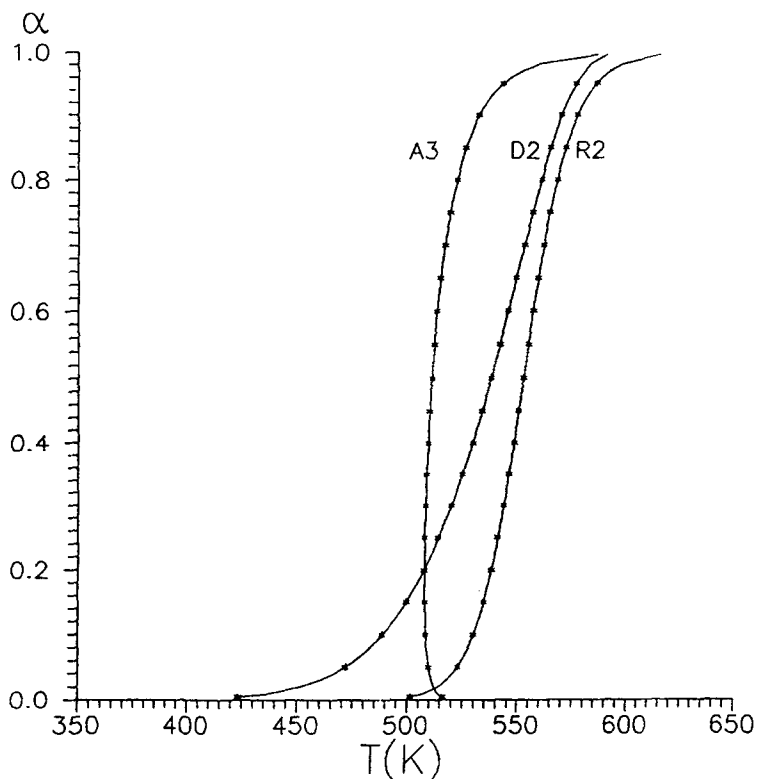


Fig. 1 Time-dependent CRTA traces obtained by assuming a R_2 , D_2 or A_3 kinetic models and the following kinetic parameter: $E = 120$ kJ/mol, $A = 10^9$ min⁻¹ and $C = 10^{-5}$ min⁻²

ergy, E , can be calculated from the apparent activation energy, E' , determined from the slope of the above plot, provided that the ratio E'/E is known (Table 2) it is noteworthy that if the reaction obeys the Avrami–Erofeev kinetic model A_2 both the slope and the intercept are infinite. Thus, in this particular case, the plot above described permits to discriminate the kinetic equation fitted by the reaction but does not supply the value of the activation energy that, however, would be calculated from Eq. (4) after substituting the $f(\alpha)$ function corresponding to the A_2 model.

Results

In order to check the above conclusions we have to consider the kinetic analysis of a series of α – T curves of solid state reactions simulated by assuming a controlled linear increase of the reaction rate. Figure 1 shows the time-dependent CRTA traces constructed by assuming that the reaction fits either a R_2 or D_2 or A_3 kinetic models, respectively. The following kinetic parameters have

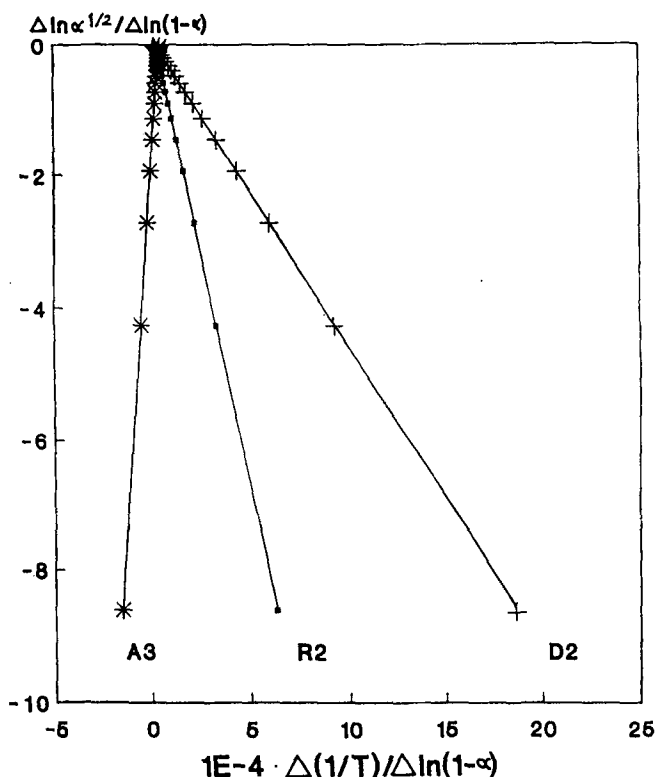


Fig. 2 Plot of data taken from Fig. 1 in agreement with Eq. (11)

Tables 3 Values of $c = E'/E$ and d determined from the plots of Fig. 2

Kinetic equation	$c = E'/E$	d	r
R_2	1.00	0.50	1.00000
D_2	0.33	0.14	1.00000
A_3	-2.97	-2.15	0.99999

been assumed: $A = 10^9 \text{ min}^{-1}$; $E = 120 \text{ kJ/mol}$ and $C = 10^{-5} \text{ min}^{-2}$. The plots of the values of $\Delta \ln \alpha^{1/2} / \Delta \ln(1 - \alpha)$ taken from the curves are included in Fig. 2. The values of $c = E'/E$ and d determined from these plots have been included in Table 3 and they are in very good agreement with those forecasted in Table 1.

In short, the above results allow to conclude that the analysis of a single α - T curve recorded under a linear increase of the reaction rate permits to discriminate the kinetic model fitted by reaction and simultaneously, to determine the activation energy of the process. Therefore, the development of equipments that allow to control the temperature of the sample according to the new method here proposed would permit a significant enhancement of the discrimination power of the kinetics models obeyed by solid state reactions from a single experiment. The development of an experimental tool to apply the described technique is now in process in our laboratory.

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Zusammenfassung — Es konnte gezeigt werden, daß die Darstellung der Werte für $\Delta \ln \alpha^{1/2} / \Delta \ln(1 - \alpha)$ (ermittelt aus einer einfachen α - T Kurve, die unter einem kontrollierten linearen Anwachsen der Reaktionsgeschwindigkeit aufgenommen wurde) als eine Funktion der entsprechenden Werte für $\Delta(1/T) / \Delta \ln(1 - \alpha)$ eine gleichzeitige Ermittlung von sowohl Aktivierungsenergie als auch des kinetischen Modelles von Feststoffreaktionen ermöglicht.