

# INFLUENCE OF THE PARTICLE SIZE DISTRIBUTION ON THE CRTA CURVES FOR THE SOLID-STATE REACTIONS OF INTERFACE SHRINKAGE TYPE

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## Abstract

The kinetic curves at infinite temperature for the solid-state reactions of the interface shrinkage type were drawn theoretically by taking account the particle size distribution in the sample mixture. The CRTA curves for the reactions with the particle size distribution can be drawn by utilizing the universal kinetic curves at infinite temperature. The proper kinetic treatment for the CRTA curves with the particle size distribution is discussed in connection with the property of the kinetic equation with respect to the particle size distribution. The present kinetic consideration is taken as a simulation for the reactions with a certain distribution in  $\alpha$  among the reactant particles, produced preferably by the mass and heat transfer phenomena during the thermoanalytical measurements. The merit of the rate jump method by a single cyclic CRTA curve is also discussed on the basis of the present results.

**Keywords:** CRTA, kinetics, particle size distribution, rate jump method

## Introduction

Characterization of the position and shape of the thermoanalytical (TA) curves has widely been examined for understanding the kinetics of solid-state reactions [1, 2], in which the following kinetic equation is assumed irrespective of the TA curves under different types of temperature change, e.g., isothermal, non-isothermal, controlled-rate thermal analytical (CRTA) [3], and so on.

$$\frac{d\alpha}{dt} = A' \exp\left(-\frac{E}{RT}\right) f(\alpha), \quad (1)$$

where  $\alpha$  and  $f(\alpha)$  are the fractional reaction and the physico-geometric kinetic model functions [4, 5], respectively. Other symbols are in standardized meanings. The function  $f(\alpha)$  is usually derived on the basis of a formal physico-chemical description of geometrically well defined reactant bodies. The macroscopic nature of TA curves averaged over the reactant particles in the sample assemblage does not always bear the strictly defined physico-geometric kinetic description [6]. The mass

and heat transfer phenomena during the TA measurement are considered as such unreliability of the TA curves as a possible source of kinetic data, producing probably a certain distribution in the  $\alpha$  among the particles in the reactant mixture. Although it is difficult to identify experimentally the distribution function of  $\alpha$  during the reaction, the situation can be simulated theoretically by assuming the size distribution of the reactant particles.

For the interface shrinkage reactions, such as the phase boundary reaction  $R_n$  and diffusion  $D_n$  controlled mechanisms, the particle size distribution (PSD) is the direct cause of the distribution in  $\alpha$  among the particles in the reactant mixture. Analyzing the TA curves, the PSD should be taken into account in order to evaluate the meaningful kinetic results. Under isothermal conditions, the PSD has been tried to incorporate in the kinetic equation [7-9]. Distortion in the apparent kinetic parameters calculated without taking account the PSD were discussed for the TA curves under linearly increasing temperature [10, 11]. Recently, we demonstrated theoretically [12] that the influence of the PSD on the kinetic curves is expressed by the unified kinetic expression at infinite temperature irrespective of the types of temperature change during the course of reaction. Because the influence of the PSD is understood as the summation of the parallel reactions with the same activation energy  $E$  and the different apparent preexponential factors  $A'$ , the universal kinetic relationship at infinite temperature [13] is maintained with the existing PSD. The confirmed fact enable us to draw the theoretical CRTA curves for the reactions with the PSD, that have never been examined because of the complex mathematical formalism.

In the present paper, the CRTA curves for the interface shrinkage type of solid-state reactions with the PSD are drawn theoretically by applying the universal kinetic relationship at infinite temperature. The proper kinetic treatment for the CRTA curves with the PSD is discussed in connection with the property of the kinetic equation. On the basis of the theoretical consideration concerning the influence of the possible distribution of  $\alpha$  on the CRTA curves, the practical usefulness of the rate jump method for determining the activation energy is also discussed.

## Theoretical

### *Incorporation of the particle size distribution*

A typical example of the size distribution of the reactant particles, the log-normal distribution law was applied in the present study, is given in Eq. (2) [14]:

$$\frac{d\Phi}{dz} = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[ -\frac{(z - \bar{z})^2}{2\sigma^2} \right] \quad \text{with } z = \ln x \quad (2)$$

where  $x$ ,  $\Phi$ ,  $\sigma$  and  $\bar{z}$  are the size of a particular geometric factor, frequency, logarithmic standard deviation and logarithmic averaged size, respectively. The distribution curves were drawn by assuming the values of  $\bar{z} = \ln(10/\mu\text{m})$  and various  $\sigma$ , where the boundaries of the abscissa were determined as the total area of the distri-

bution curves being better than 99.9%. The distribution curve is divided into  $n$  slices, parallel to the vertical axis with equivalent spacing on the abscissa. The averaged size in the respective slice,  $\bar{x}_m$ , is used for determining the fractional reaction in the  $m$ -th slice,  $\bar{\alpha}_m$ .

The following kinetic equations are assumed for the respective reactant particles under isothermal and linearly increasing temperature conditions, respectively.

$$\bar{s}_m g(\bar{\alpha}_m) = kt \quad \text{with} \quad k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

$$\bar{s}_m g(\bar{\alpha}_m) = \frac{AE}{\beta R} \frac{\exp(-u)}{u} \pi(u)$$

$$\text{with} \quad \pi(u) = \frac{u^3 + 18u^2 + 88u + 96}{u^4 + 20u^3 + 120u^2 + 120} \quad \text{and} \quad u = \frac{E}{RT} \quad (4)$$

where  $\bar{s}_m$ ,  $g(\bar{\alpha}_m)$  and  $\beta$  are the averaged geometric size coefficient [12] in the  $m$ -th slice, kinetic model function in integral form and heating rate, respectively. The function  $\pi(u)$  is an approximation function of exponential temperature integral proposed by Senum and Yang [15]. By assuming the Arrhenius parameters,  $E = 100 \text{ kJ mol}^{-1}$  and  $\ln A = 20 \text{ } \mu\text{m s}^{-1}$ , and various  $g(\alpha)$ , the isothermal and non-isothermal kinetic curves for the respective slices were drawn for the constant temperature  $T$  and  $\beta$ , respectively. The overall fractional reaction  $\alpha$  at time  $t$  or  $T$  for the system with a particular PSD are obtained according to the equation:

$$\alpha = \sum_{m=1}^n \bar{\alpha}_m \left(\frac{dV}{V}\right)_m \quad (5)$$

where  $(dV/V)_m$  is the volume fraction of the reactant particles in the  $m$ -th slice. The isothermal and non-isothermal kinetic curves for the solid-state reactions with a particular PSD were drawn by plotting the  $\alpha$  vs.  $t$  and  $T$ , respectively.

#### *Universal kinetic relationship at infinite temperature*

In our previous study [12], it was shown theoretically that the value of  $E$  maintains constant with respect to the overall  $\alpha$  for the system with the PSD, proved through applying the isoconversion methods [16]. Using the value of  $E$ , the overall rate behavior taking account the PSD is extrapolated to infinite temperature in the same way with the ideal reaction of the uniformly sized particles [17]. The reaction rate at infinite temperature is expressed by

$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt} \exp\left(\frac{E}{RT}\right) = A''h(\alpha)$$

$$\text{with } \theta = \int_0^t \exp\left(-\frac{E}{RT}\right) dt \quad (6)$$

where  $\theta$ ,  $A''$  and  $h(\alpha)$  are the generalized time [18], apparent preexponential factor for the overall reaction and empirical kinetic model function which describes the apparent shape of the kinetic curve, respectively.

### Theoretical drawing of the CRTA curves

The CRTA curves are characterized by the constant transformation rate during the course of reaction [3]. Knowing the universal kinetic curves at infinite temperature, the theoretical CRTA curves can be drawn by applying the pre-determined constant transformation rate,  $C=d\alpha/dt$ , and value of  $E$  into Eq. (6).

## Results and discussion

### Apparent CRTA curves

Figure 1 shows the universal kinetic curves at infinite temperature for various interface shrinkage reactions with the log-normal PSD of  $\sigma=0.5$ , as the plots of  $d\alpha/d\theta$  vs.  $\alpha$ . It was already shown [12] that with increasing the PSD the shape of the  $d\alpha/d\theta$  vs.  $\alpha$  plot deviates readily from the characteristic shapes for the respective kinetic models. The CRTA curves for the  $R_3$  and  $D_4$  models with various  $\sigma$  are shown in Fig. 2. With increasing  $\sigma$ , the CRTA curves shift to the higher temperature by widening the reaction temperature region. The similar behavior was observed for all the other kinetic models of reaction interface shrinkage type, as is the case of the TA curves under linearly increasing temperature.

According to Eq. (1), the CRTA curves were subjected to the kinetic plot of the conventional differential single run method by assuming the kinetic model of the

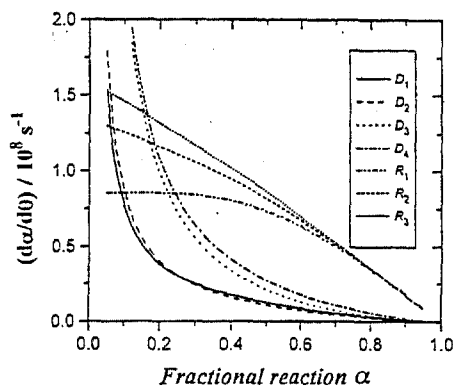


Fig. 1 The plots of  $d\alpha/d\theta$  vs.  $\alpha$  for various interface shrinkage reactions with  $\sigma=0.5$

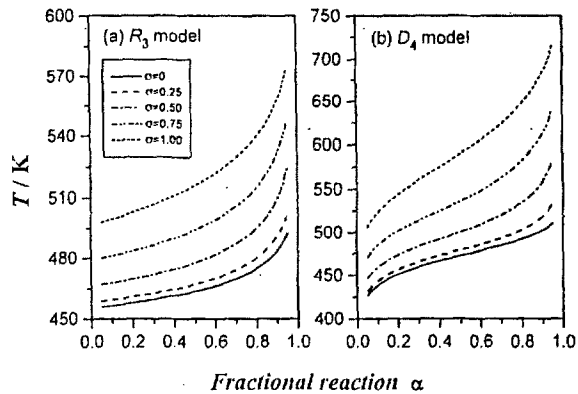


Fig. 2 The CRTA curves for the  $R_3$  and  $D_4$  reactions with  $C=1.0 \times 10^{-3} \text{ s}^{-1}$  and various  $\sigma$

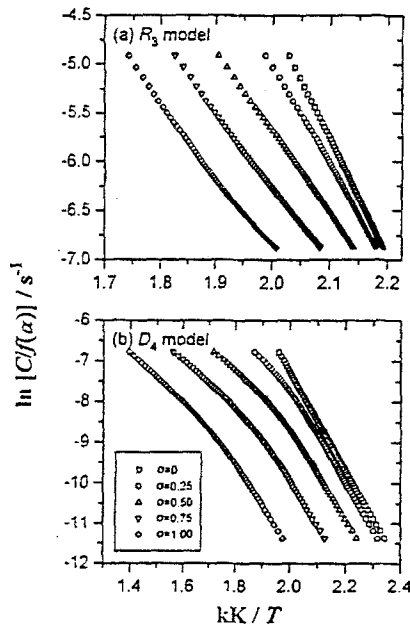


Fig. 3 The plots of  $\ln[C/f(\alpha)]$  vs.  $T^{-1}$  for the respective CRTA curves shown in Fig. 2

single particle, i.e., the plot of  $\ln[C/f(\alpha)]$  vs.  $T^{-1}$ . Figure 3 shows the kinetic plots within the restricted range  $0.05 \leq \alpha \leq 0.95$ . With increasing  $\sigma$ , the kinetic plot for the CRTA curves with PSD deviates from the ideal plot by decreasing the slope and increasing the curvature. It is apparent that the meaningful kinetic parameters based on the physico-geometry of the reaction can not be obtained from the single run method without taking account the PSD.

### Kinetic analysis

If a series of the CRTA curves of the different constant rates were available, the Friedman method [19], the differential isoconversion method, is applicable for obtaining the value of  $E$  at various  $\alpha$ . Figure 4 shows the typical Friedman plots at  $\alpha=0.5$  for the CRTA curves of the  $R_3$  reaction with various  $\sigma$ . Any changes in the slope with PSD are not observed, providing the correct value of  $E$ . At infinite temperature, the overall  $\alpha$  for the interface shrinkage reaction with PSD is expressed as

$$\alpha = \sum_{m=1}^n \left[ \left( \frac{dV}{V} \right)_m G \left( \frac{A\theta}{s_m} \right) \right]_{T=\infty} \quad (7)$$

where  $G$  is the anti-function of the  $g(\overline{\alpha}_m)$ . Because Eq. (7) holds for the kinetic data under any temperature changes unless the kinetic term  $G(A\theta/s_m)$  remains constant among the series of kinetic curves with different transformation rates, the kinetic relation with respect to the PSD is canceled for the selected  $\alpha$ . The rate jump method [20] utilized for obtaining the  $E$  value from a single cyclic CRTA curve is equally useful for the reaction with PSD, regarding as an approximated isoconversion method.

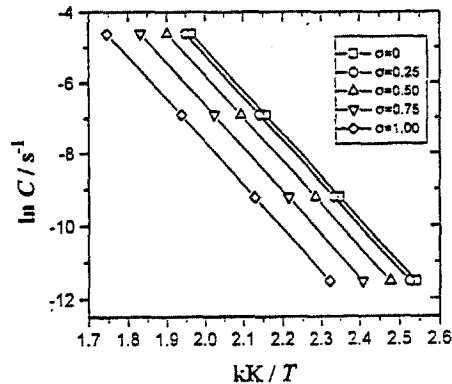


Fig. 4 Typical Friedman plots for the CRTA curves of the  $R_3$  reaction with various  $\sigma$  at  $\alpha=0.5$

The kinetic curves with PSD at infinite temperature, Fig. 2, can be reproduced from the intercepts of the Friedman plots at various  $\alpha$ . The integral kinetic curves at infinite temperature are obtained by the numerical integration [13].

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{h(\alpha)} = A'' \int_0^{\theta} d\theta = A''\theta \quad (8)$$

Figure 5 shows the integral kinetic curves at infinite temperature of the  $R_3$  and  $D_4$  reactions with various  $\sigma$ , as the plots of  $\alpha$  vs.  $\theta$ . For the reactant assemblage with

well defined PSD, the value of  $A$  at the selected  $\theta$  is determined by taking account Eq. (7) using a computer method of simplex optimization [12] according to the integral kinetic curve at infinite temperature, Fig.5. The best value of  $A$  at a given  $\theta$  for the assumed integral kinetic model function  $g(\alpha)$  is determined by minimizing the square of the difference between the calculated value of  $\alpha$  at the selected  $\theta$  and the value read from the kinetic curve. The constant value of  $A$  during the course of reaction is obtained when the correct  $g(\alpha)$  for a single particle were used for calculation.

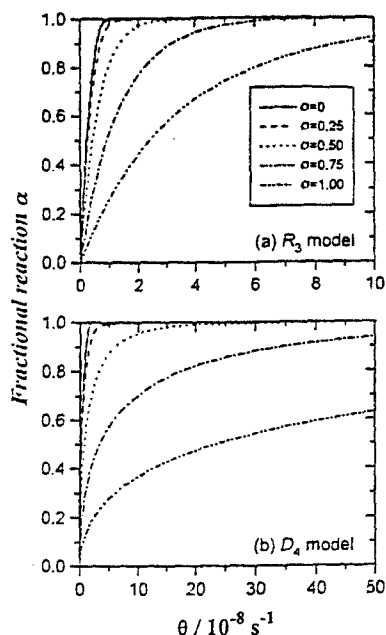


Fig. 5 The plots of  $\alpha$  vs.  $\theta$  of the  $R_3$  and  $D_4$  reactions with various  $\sigma$

It was already shown [12] that the distinction of the appropriate  $g(\alpha)$  through the determination of the  $A$  value depends on the degree of PSD. With increasing PSD, the possibility of the kinetic model discrimination decreases within the same group of the  $g(\alpha)$ , the  $R_n$  or  $D_n$ , because the shape of the kinetic plots at infinite temperature converges to the characteristic shape of the respective groups of the kinetic model [12]. For the practical kinetic analysis taking account the PSD, it is required to investigate previously the possibility of the kinetic model discrimination at the given PSD.

As was discussed above, even for the reactions with a certain distribution in  $\alpha$  among the respective particles, the reliable activation energy is obtained by one of the isoconversion methods. In CRTA, the series of kinetic curves with different overall reaction rates can be obtained by changing the controlled transformation rate or the sample mass in remaining the other experimental conditions constant. Through the CRTA measurements for the thermal decomposition of calcium carbonate [21], it was indicated recently that the influence of the mass transfer phe-

nomena during the reaction can be controlled to be constant only within the limited range of sample mass. In this respect, a single cyclic CRTA has a merit to maintain the  $\alpha$  distribution constant between the two adjacent data points of different decomposition rates, at least, compared with the series of CRTA curves with different sample masses or controlled transformation rates. This seems to be one of the reasons for the reliable determination of the activation energy by the rate jump method from a single cyclic CRTA curve [22].

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