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Kinetic Analysis of Solid-State Reactions: The Universality of Master Plots for Analyzing Isothermal and Nonisothermal Experiments

Francisco J. Gotor,[†] José M. Criado,*[,†] Jiri Malek,[‡] and Nobuyoshi Koga[§]

Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, 41092 Sevilla, Spain, Joint Laboratory of Solid State Chemistry of the Academy of Sciences of the Czech Republic and University of Pardubice, 530 09 Pardubice, Czech Republic, and Chemistry Laboratory, Faculty of Education, Hiroshima University, Higashi-Hiroshima 739-8524, Japan

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Master plot methods based on the integral and/or the differential forms of the kinetic equation describing solid-state reactions have been redefined by using the concept of the generalized time, θ, introduced by Ozawa. This redefinition permits the application of these master plots to the kinetic analysis of solid-state reactions, whatever the type of temperature program used for recording the experimental data. In isothermal conditions, a single curve is enough to construct the experimental master plots. In nonisothermal conditions, the knowledge of both α as a function of temperature and activation energy is required for calculating the master plot curves from the experimental data. Practical usefulness of the present master plot methods is examined, and exemplified by being applied to the thermal decomposition of $ZnCO_3$ under isothermal, linear nonisothermal, and nonlinear nonisothermal conditions.

1. Introduction

The kinetic analysis of solid-state reactions from experimental thermoanalytical (TA) data recorded under nonisothermal conditions became very popular from the earlier proposals by Kissinger,[1] Freeman and Carroll,[2] Coats and Redfern,[3] and Zakó[4] of formal kinetic equations to be used for this purpose. Many methods have been subsequently developed, but the opinion that most of the research devoted to the proposal of these new methods has been useful for producing a huge number of publications rather than for leading to a better knowledge of the mechanism of solid-state reactions is very extended. The popularity of the nonisothermal methods with regard to the isothermal ones rests on the assumption that the reaction kinetic parameters can be determined from a single nonisothermal experiment while isothermal methods require a set of experiments at different temperatures. However, it has been pointed out in previous papers[5,6] that both the kinetic parameters and the kinetic model obeyed by the reaction cannot be simultaneously discriminated from a single experiment. It would be interesting to introduce a new point of view for the kinetic study of solid-state reactions that would lead to the simultaneous analysis of isothermal and nonisothermal data and to establish the minimum number of independent experiments required for determining the kinetic model of the reaction. This finding would give a global view of isothermal and nonisothermal experiments.

Several attempts have been made to determine the physico-geometric mechanism of solid-state reactions by using the so-called "master plot".[7−20] Master plots are reference theoretical curves depending on the kinetic model but generally independent of the kinetic parameters of the process. Because, in many cases, the experimental kinetic data can easily be transformed to the experimental master plots, comparison of the theoretical master plots drawn by assuming various kinetic models with the experimental master plot allows us to select the appropriate kinetic model of the process under investigation or, at least, of the type of appropriate kinetic models. The knowledge of the kinetic model, deduced from such a simple graphical method, is very helpful for further detailed kinetic analysis by avoiding a possible misestimation of the kinetic parameters due to the wrong kinetic model being assumed.[21,22]

Because independence from the measured temperature conditions is another important characteristic of the master plot, various master plot methods have been proposed individually for the kinetic data recorded under different types of temperature programs, such as for isothermal,[7−13] linear nonisothermal,[14−18] and nonlinear nonisothermal[19,20] measurements. A very extended method, developed by Sharp et al.[8] for isothermal data, is the reduced-time master plot that represents the reacted fraction, α, at time t versus reduced time, $t/t_{0.5}$ ($t_{0.5}$ being the time at which $\alpha = 0.5$). The curves for all kinetic models coincide at $t/t_{0.5} = 1$, but reasonably large differences in the shape of the master plots are at once apparent among different kinetic models. Among the master plot methods for nonisothermal data, we can cite those based on the first or second derivative of α.[17,18] In many cases for the linear nonisothermal kinetic data, however, the reaction mechanism cannot be ascertained from only one nonisothermal experiment unless one of the kinetic parameters, i.e., the activation energy E or preexponential factor A, is known, because of the interdependence of the assumed kinetic model with calculated kinetic parameters.[21−23]

The kinetic use of the recently developed thermoanalytical techniques under nonlinear nonisothermal conditions such as temperature-modulated and sample-controlled measurements is growing quickly. Two different types of reduced-temperature master plots based on the integral and differential kinetic equations have already been proposed for the kinetic data recorded by constant-rate thermal analysis (CRTA).[19,20] The

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* To whom correspondence should be addressed. Fax: (34) 954460665. E-mail: jmcriado@cica.es.

[†] Centro Mixto CSIC-Universidad de Sevilla.

[‡] Academy of Sciences of the Czech Republic and University of Pardubice.

[§] Hiroshima University.

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TABLE 1: Algebraic Expressions for the *f*(α) and *g*(α) Functions for the Most Common Mechanisms in Solid-State Reactions

mechanism	symbol	$f(\alpha)$	$g(\alpha)$
phase boundary controlled reaction (contracting area, i.e., bidimensional shape)	R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
phase boundary controlled reaction (contracting volume, i.e., tridimensional shape)	R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$
unimolecular decay law (instantaneous nucleation and unidimensional growth)	F1	$(1-\alpha)$	$-\ln(1-\alpha)$
random nucleation and growth of nuclei (Johnson−Mehl−Avrami equation)[a]	Am	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	$[-\ln(1-\alpha)]^{1/m}$
two-dimensional diffusion (bidimensional particle shape)	D2	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha)+\alpha$
three-dimensional diffusion (tridimensional particle shape) (Jander equation)	D3	$\dfrac{3(1-\alpha)^{2/3}}{2[(1-\alpha)^{1/3}]}$	$[1-(1-\alpha)^{1/3}]^2$
three-dimensional diffusion (tridimensional particle shape) (Ginstein−Brounshtein equation)	D4	$\dfrac{3}{2[(1-\alpha)^{-1/3}-1]}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

[a] This formal kinetic law generally applies for random nucleation and growth of nuclei, although they are two different processes with different kinetic parameters. The nuclei are generally formed during the induction period. Thus, the α−*t* (or *T*) plots usually represent the growth process from preexisting nuclei.

CRTA method implies the reaction temperature should be controlled in such a way that both the reaction rate and the partial pressure of the gases produced or consumed in the reaction are maintained at any constant previously selected value. This experimental method allows minimizing the influence of heat- and mass-transfer phenomena on the forward reaction.[24,25] This method has also been successfully used for the synthesis of materials with controlled texture and structure.[26−29]

A comparison of the kinetic results for a process under different types of temperature programs is essential for a systematic kinetic analysis of the solid-state reactions, which enables us to evaluate the reliability of the kinetic results and/or to investigate further detailed kinetic characteristics of the process.[24] Development of a master plot method applicable universally to the experimental kinetic data under any type of temperature program is thus desired for comparing the physicogeometric mechanism of a process under different temperature profiles. For this purpose, the generalized kinetic equations proposed by Ozawa[14,15] seem to be very useful. By introducing the generalized time, θ,[14,15,30] Ozawa constructed the generalized kinetic equation at infinite temperature originally for analyzing the kinetic data under linearly increasing temperature. Because the kinetic data recorded under any temperature profile can be extrapolated to infinite temperature by using the predetermined value of E,[31,32] the generalized kinetic equations can be used even for the kinetic analysis of the nonlinear nonisothermal data such as CRTA.[25,33] At the same time, the universal property of the generalized kinetic equations makes it possible to calculate the rate behavior under any temperature profile from the extrapolated rate data using the predetermined value of E.[14,34,35]

In the present work, on the basis of the generalized kinetic equations at infinite temperature, we have redefined a series of master plot methods applicable universally to the kinetic analysis of solid-state reactions from TA data under any type of temperature profile. The procedures for calculating the experimental master plots are described with reference to the conventional master plot methods. To evaluate the practical usefulness, the theoretical conclusions have been applied to the experimental data of the thermal decomposition of $ZnCO_3$ recorded under various types of temperature profiles. The practical roles of the universal master plot methods throughout the systematic kinetic analysis are discussed as concluding remarks.

2. Theory

2.1. Generalized Kinetic Equations. The rate of a solid-state reaction can be expressed by means of the following general law:

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

α is the reacted fraction at time t, $f(\alpha)$ a function depending on the reaction mechanism (Table 1), E the activation energy, A the preexponential factor of Arrhenius, and T the absolute temperature. The kinetic rate equation at infinite temperature is obtained by introducing the generalized time θ defined as[14,15,30]

$$\theta = \int_0^t \exp\left(-\frac{E}{RT}\right) dt \qquad (2)$$

where θ denotes the reaction time taken to attain a particular α at infinite temperature. Differentiation of eq 2 leads to[15,30]

$$\frac{d\theta}{dt} = \exp\left(-\frac{E}{RT}\right) \qquad (3)$$

Combining eqs 1 and 3, the following expression is obtained:[15,30]

$$\frac{d\alpha}{d\theta} = Af(\alpha) \qquad (4)$$

or

$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt}\exp\left(\frac{E}{RT}\right) \qquad (5)$$

where $d\alpha/d\theta$ corresponds to the generalized reaction rate, obtained by extrapolating the reaction rate in real time, $d\alpha/dt$, to infinite temperature. The integrated form of the kinetic rate equation is obtained from eq 4 as follows:[14,30]

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A\int_0^\theta d\theta = A\theta \qquad (6)$$

2.2. Master Plots Based on the Differential Form of the Generalized Kinetic Equation. Using a reference point at $\alpha = 0.5$, the following equation is easily derived from eq 4:

$$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}} = \frac{f(\alpha)}{f(0.5)} \tag{7}$$

where $f(0.5)$ is a constant for a given kinetic model function. Equation 7 indicates that, at a given α, the experimentally determined value of the reduced−generalized reaction rate, $(d\alpha/d\theta)/(d\alpha/d\theta)_{\alpha=0.5}$, and theoretically calculated value of $f(\alpha)/f(0.5)$ are equivalent when an appropriate $f(\alpha)$ for describing the rate process under investigation is applied. Because both the values depend only on α, comparison of the experimental plot of $(d\alpha/d\theta)/(d\alpha/d\theta)_{\alpha=0.5}$ against α with the theoretical plots of $f(\alpha)/f(0.5)$ against α, drawn by assuming various $f(\alpha)$ functions, is methodologically identical to the conventional master plot method. Figure 1 shows the theoretical master plots of $f(\alpha)/f(0.5)$ against α, drawn by assuming various $f(\alpha)$ functions listed in Table 1. The theoretical master plots of all $f(\alpha)$ functions coincide at $\alpha = 0.5$ and disperse clearly among different $f(\alpha)$ functions in the range of $\alpha < 0.5$.

According to eq 5, the reduced−generalized reaction rate has the following relationship to the experimental kinetic data:

$$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}} = \frac{d\alpha/dt}{(d\alpha/dt)_{\alpha=0.5}} \frac{\exp(E/RT)}{\exp(E/RT_{0.5})} \tag{8}$$

where $T_{0.5}$ is the reaction temperature at $\alpha = 0.5$. For calculating the experimental value of $(d\alpha/d\theta)/(d\alpha/d\theta)_{\alpha=0.5}$, the temperature conditions of the experimental kinetic data have to be taken into account. For the experimental kinetic data under isothermal conditions, both the exponential terms in eq 8 offset each other because $T = T_{0.5}$, so that the experimental master plot can be derived directly from a single isothermal curve of $d\alpha/dt$ against α.

On the other hand, for all nonisothermal data, the exponential terms in eq 8 cannot be canceled out. For calculating the reduced−generalized reaction rate at a given α from nonisothermal data under linear and nonlinear heating, in addition to the kinetic data of a single measurement, the value of E for the process should be known previously. As a special case of the nonlinear nonisothermal data, the ratio of rate terms in real time in eq 8 is to be unity for the kinetic data of CRTA.

2.3. Master Plots Based on the Integral Form of the Kinetic Data. From the integral kinetic equation at infinite temperature in integral form, eq 6, we can obtain the following equation using a reference point at $\alpha = 0.5$:[36,37]

$$\frac{g(\alpha)}{g(0.5)} = \frac{\theta}{\theta_{0.5}} \tag{9}$$

where $\theta_{0.5}$ is the generalized time at $\alpha = 0.5$. As in the case of the differential master plot method based on eq 7, the integral master plot method at infinite temperature can be constructed by comparing the experimental master plot of the reduced−generalized time, $\theta/\theta_{0.5}$, against α with various theoretical master plots of $g(\alpha)/g(0.5)$ against α. Figure 2 shows the theoretical master plots of various $g(\alpha)$ functions. The master plots coincide with $g(\alpha)/g(0.5) = 0$ at $\alpha = 0$ and $g(\alpha)/g(0.5) = 1$ at $\alpha = 0.5$, but reasonably large differences among different $g(\alpha)$ functions assumed are apparent within the range $\alpha > 0.5$. The ranges of α, where the theoretical master plots of different kinetic models are clearly distinguished, are $\alpha < 0.5$ and $\alpha > 0.5$ for the differential and integral master plots, respectively. By following the two master plot methods, the kinetic agreement with a particular kinetic model function during the whole course of the process can be examined.

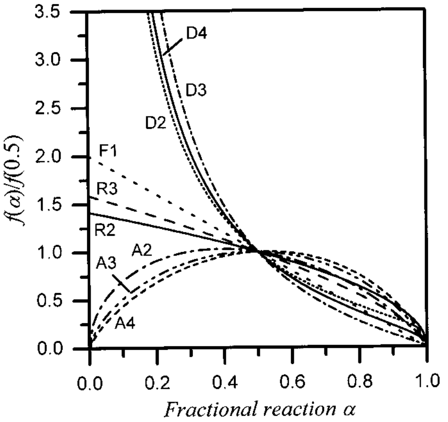

Figure 1. Theoretical master curves in differential form representing $f(\alpha)/f(0.5)$ as a function of α for the different kinetic models describing solid-state reactions.

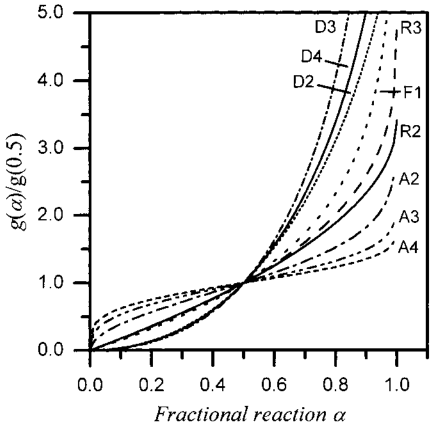

Figure 2. Theoretical master curves in integral form representing $g(\alpha)/g(0.5)$ as a function of α for the different kinetic models describing solid-state reactions.

From the kinetic data under isothermal conditions, eq 2 can be expressed as[31]

$$\theta = \exp\left(-\frac{E}{RT}\right)t \tag{10}$$

Because the exponential term in eq 10 is a constant during the course of the reaction, the value of $\theta/\theta_{0.5}$ at a given α is equivalent to $t/t_{0.5}$. Equation 9 is then transformed into

$$\frac{g(\alpha)}{g(0.5)} = \frac{t}{t_{0.5}} \tag{11}$$

Equation 11 is identical to the master plot method developed by Sharp et al.[8] for the kinetic data under isothermal conditions. Accordingly, a single isothermal kinetic curve of α against t is enough to calculate the experimental master plot of $\theta/\theta_{0.5}$ against α.

In nonisothermal conditions, solving the integral defined in eq 2 requires the knowledge of the time dependence of temperature. From the kinetic data under a linear heating rate of β, the value of θ at a given α can be calculated by

$$\theta = \frac{1}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E}{\beta R}\int_x^\infty \frac{\exp(-x)}{x^2}\, dx = \frac{E}{\beta R}p(x) \tag{12}$$

where $x = E/RT$. The function $p(x)$ cannot be expressed in a closed form, although several convergent series exist for its approximation. For example, the fourth rational approximation of Senum and Yang,[38] corrected recently by Flynn,[39] allows an accuracy of better than $10^{-5}\%$ for $E/RT = 20$:

$$p(x) = \frac{e^{-x}}{x}\pi(x) \tag{13}$$

and

$$\pi(x) = \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{14}$$

For a linear heating rate, therefore, the $\theta/\theta_{0.5}$ values can be calculated from the following equation:

$$\frac{\theta}{\theta_{0.5}} = \frac{p(x)}{p(x_{0.5})} \tag{15}$$

The knowledge of α as a function of temperature and the value of E is then required for calculating the experimental master plot of $\theta/\theta_{0.5}$ against α from experimental data obtained under a linear heating program.

On the other hand, for other nonisothermal processes where the time dependence of the temperature is not simple (or not known) such as in CRTA, stepwise isothermal analysis (SIA) or high-resolution thermogravimetry (HRTG), it is not possible to calculate the values of θ directly from the experimental kinetic data. As a practical method of calculating the value of θ from the kinetic data under nonlinear nonisothermal conditions, a numerical calculation based on the differential kinetic data at infinite temperature has been examined.[32] As was described above, knowing previously the value of E, the differential kinetic data at infinite temperature, $d\alpha/d\theta$ versus α, can be calculated from the kinetic data under any temperature profile. For the numerical calculation of θ, a kind of fitting function $h(\alpha)$ is applied to the kinetic data of $d\alpha/d\theta$ against α, which is expressed as

$$\frac{d\alpha}{d\theta} \approx h(\alpha) \tag{16}$$

The values of θ can be obtained approximately by integrating numerically the reciprocal of $h(\alpha)$ according to

$$\theta = \int_0^\theta d\theta \approx \int_0^\alpha \frac{d\alpha}{h(\alpha)} \tag{17}$$

where the boundary conditions of integrating the reciprocal of $h(\alpha)$ should be taken into account.[40] For this purpose, any kind of empirical fitting function can be applied, in addition to a sophisticated empirical kinetic model function such as the Sestak−Berggren model.[41]

2.4. Master Plots Based on Both the Integral and Differential Forms of the Kinetic Equation. An alternative expression of the kinetic equation at infinite temperature can be obtained by multiplying the differential form of the kinetic equation, eq 4, by the integral kinetic equation, eq 6:[18,34,42]

$$\theta\frac{d\alpha}{d\theta} = f(\alpha)\, g(\alpha) \tag{18}$$

Because both the values of $\theta(d\alpha/d\theta)$ and $f(\alpha)\, g(\alpha)$ depend only on α, on the basis of eq 18, an alternative master plot method can be constructed by comparing the experimental master plot of $\theta(d\alpha/d\theta)$ against α and the theoretical master plots of $f(\alpha)\, g(\alpha)$ against α drawn by assuming various kinetic model functions. Figure 3 shows the theoretical master plots of $f(\alpha)\, g(\alpha)$ against α drawn by assuming various kinetic model functions listed in Table 1. The theoretical master plots of the respective kinetic models are distinguished clearly by comparing the shape, peak height, and position of the peak maximum.

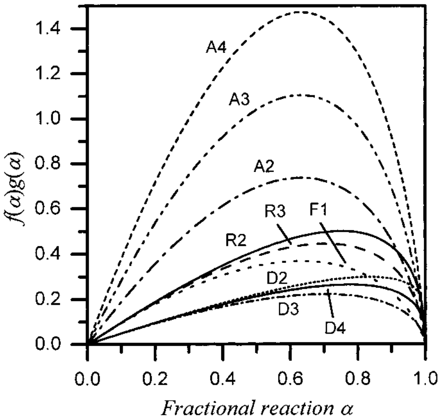

Figure 3. Theoretical master curves in differential−integral form representing $f(\alpha)\, g(\alpha)$ as a function of α for the different kinetic models describing solid-state reactions.

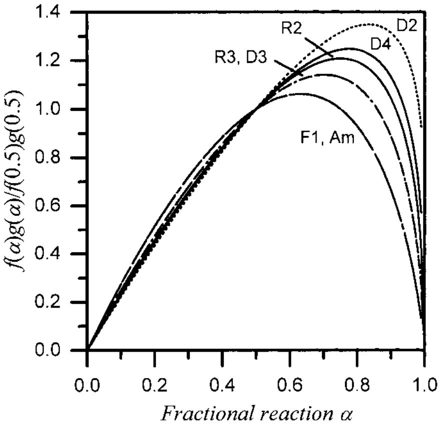

Figure 4. Theoretical master curves in differential−integral form representing $[f(\alpha)\, g(\alpha)]/[f(0.5)\, g(0.5)]$ as a function of α for the different kinetic models describing solid-state reactions.

If we present these master plots in a way similar to that of the former differential and integral ones, e.g., utilizing the reference point at $\alpha = 0.5$, we obtain by multiplying eq 7 by eq 9

$$\frac{\theta(d\alpha/d\theta)}{\theta_{0.5}(d\alpha/d\theta)_{\alpha=0.5}} = \frac{f(\alpha)\, g(\alpha)}{f(0.5)\, g(0.5)} \tag{19}$$

These theoretical master curves are shown in Figure 4. In this case, it is not possible to distinguish between the mechanisms R3 and D3 nor between a first-order reaction and the Avrami family.

The experimental master plot of $\theta(d\alpha/d\theta)$ against α can be obtained by just multiplying the values of $d\alpha/d\theta$ and θ at a given α, which have already been calculated for constructing the differential and integral master plots, respectively.

3. Results and Discussion

The practical usefulness of the master plots described above was examined by using the experimental data of the isothermal mass-loss trace, TG, and CRTA for the thermal decomposition of $ZnCO_3$ (smithsonite) under vacuum reported in a previous paper.[24] It was clarified in the previous study[24] that the

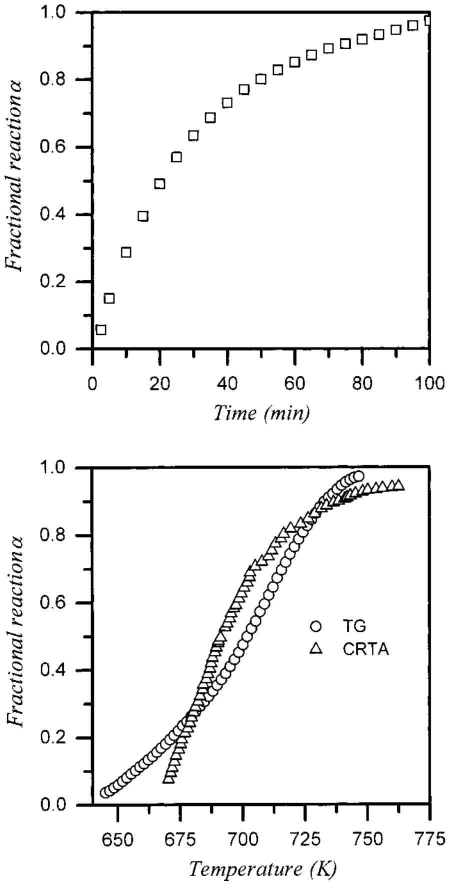

Figure 5. (a, top) Isothermal mass-loss trace at $T = 699$ K and (b, bottom) TG ($\beta = 0.57$ K min^{-1}) and CRTA (decomposition rate $C = 5.14 \times 10^{-3}$ min^{-1}) curves for the thermal decomposition of $ZnCO_3$.[24]

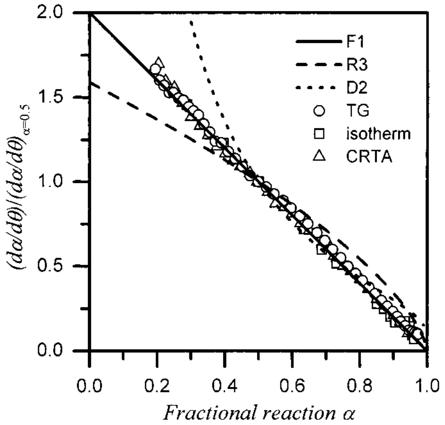

Figure 6. A comparison of the experimental master plots of $(d\alpha/d\theta)/(d\alpha/d\theta)_{0.5}$ against α for the thermal decomposition of $ZnCO_3$ with the theoretical master curves of $f(\alpha)/f(0.5)$ against α.

decomposition of $ZnCO_3$ under high vacuum at temperatures higher than 690 K fitted an F1 kinetic model with $E = 140$ kJ mol^{-1}. Figure 5 shows the kinetic curves for the thermal decomposition of $ZnCO_3$ obtained from CRTA, TG, and isothermal mass-loss measurements that appeared in ref 24.

Figure 6 compares the theoretical master plots of $f(\alpha)/f(0.5)$ against α with the experimental master plots of $(d\alpha/d\theta)/(d\alpha/d\theta)_{\alpha=0.5}$ versus α calculated from the experimental data of Figure 5. Because the exponential terms in eq 8 can be neglected for the isothermal kinetic data, the experimental master plot for the isothermal kinetic data was obtained as $(d\alpha/dt)/(d\alpha/dt)_{\alpha=0.5}$ against α. For calculating the experimental master plots for TG and CRTA data, the previously determined value of $E = 140$ kJ mol^{-1} was assumed. It is clearly seen from Figure 6 that, irrespective of the temperature profiles of the kinetic data, the experimental master plots are in good agreement with the theoretical master plot corresponding to the F1 mechanism as was determined in the previous study.[24] The master plots corresponding to the D2 and R3 models are also shown for comparison. Because, with knowledge of the value of E, the experimental master plot in differential form can be constructed from the experimental kinetic data under any temperature profile, it is very useful to check the constancy and/or variation of the reaction mechanism of the solid-state reactions under different types of temperature conditions.

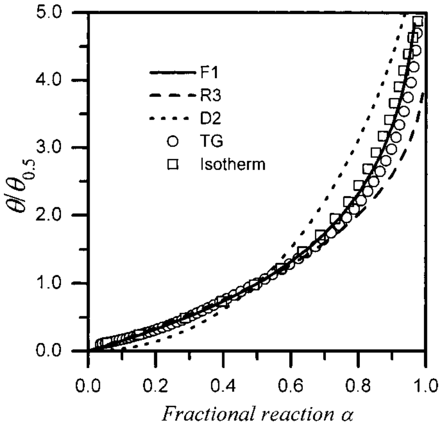

Figure 7. A comparison of the experimental master plots of $\theta/\theta_{0.5}$ against α for the thermal decomposition of $ZnCO_3$ with the theoretical master curves of $g(\alpha)/g(0.5)$ against α.

The experimental master plots of $\theta/\theta_{0.5}$ against α constructed from the experimental isothermal and TG data of Figure 5 are shown in Figure 7. The master plot for the isothermal mass-loss trace was calculated using eq 11 as $t/t_{0.5}$ against α. Using the predetermined value of $E = 140$ kJ mol^{-1}, the experimental master plot for the TG data was constructed according to eq 15. These experimental master plots obtained for the thermal decomposition of $ZnCO_3$ are compared in the same figure with the theoretical master plot corresponding to the F1 kinetic model, indicating a close agreement irrespective of quite different temperature programs. As mentioned above, it is not possible to construct this kind of master plot directly from experimental CRTA curves. On the other hand, the integral kinetic relation at infinite temperature as expressed by eq 6 is essentially important for the practical kinetic analysis, because, through the relationship, the experimental kinetic data under any temperature profile can be transformed to fractional conversion versus real time data under isothermal conditions.[14,15,30,31,43] Considering the experimental reliability of CRTA data for kinetic analysis of the solid-state reactions,[24,25,44] it is desirable to establish with wider comprehension and higher precision the practical method of numerical integration of differential kinetic data at infinite temperature for obtaining the integral kinetic data at infinite temperature.[32]

The differential−integral master plots, $\theta(d\alpha/d\theta)$ versus α, constructed from the experimental isothermal and TG data of Figure 5 are shown in Figure 8, which were obtained by multiplying the values of $d\alpha/d\theta$ and θ at a given α. The experimental master plots for isothermal and linear nonisothermal data fit again very well the theoretical curve of $f(\alpha)\ g(\alpha)$ against α corresponding to an F1 kinetic model.

As exemplified by being applied to the thermal decomposition of $ZnCO_3$ under isothermal, linear nonisothermal, and nonlinear nonisothermal conditions, the master plot methods based on the

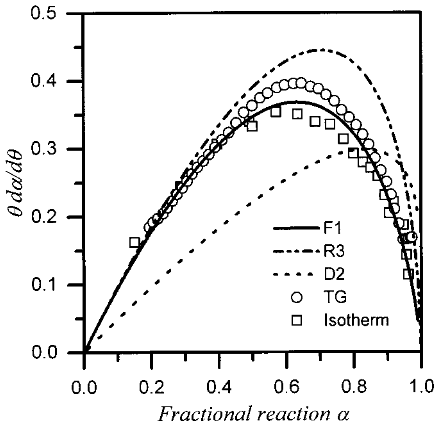

Figure 8. A comparison of the experimental master plots of $(d\alpha/d\theta)\theta$ against α for the thermal decomposition of $ZnCO_3$ with the theoretical master curves of $f(\alpha)\ g(\alpha)$ against α.

kinetic relationship at infinite temperature by a simple graphical method are practically useful to compare the influence of the types of temperature profiles on the reaction kinetics. An appropriate kinetic model can be distinguished equally by each of these three methods. Such a first-find estimation of the appropriate kinetic model is very helpful for further detailed kinetic analysis.

4. Conclusions

By using the concept of generalized time θ, we have reexamined some of the master plot methods developed in the literature. More precisely, we have focused on those based on the integral and/or differential forms of the general kinetic equation at infinite temperature. It has been shown that the three master plots redefined in this work have a universal character and they can be applied to the kinetic analysis of solid-state reactions, whatever the temperature program used for recording the experimental data.

The results shown both in the theoretical and experimental parts lead to the following conclusions.

(1) A single α (and/or $d\alpha/dt$) versus t curve obtained under isothermal conditions permits the kinetic model fitted by the studied reaction to be discerned. Obviously, a further detailed kinetic analysis is required for determining the kinetic parameters. This can be done from a series of α-t curves recorded under isothermal conditions.

(2) For experimental data obtained under a linear heating rate, the knowledge of both α as a function of temperature and activation energy is required to construct the experimental master plots. The activation energy could be determined from a series of TG or DTG curves recorded at different heating rates by using isoconversional methods such as Kissinger,[1] Ozawa,[14] or Friedman[45] without previous assumptions regarding the kinetic model fulfilled by the reaction.

(3) Master plot methods based on the integral form of the kinetic equation can only be applied directly to experimental data obtained under experimental conditions for which the time dependence of the temperature is known. On the other hand, the $(d\alpha/d\theta)/(d\alpha/d\theta)_{\alpha=0.5}$ versus α master plot, i.e., based on the differential form of the kinetic equation, can be considered as the most general because it can be applied to experimental data recorded under any experimental condition. The universal characteristics of the master plot methods enable us to compare the change in the kinetic agreement to a particular kinetic model with the applied types of temperature conditions, i.e., isothermal, linear nonisothermal, and nonlinear nonisothermal. In any case, for nonisothermal conditions, the knowledge of α as a function of temperature and activation energy is required for calculating the experimental master plots from the experimental data. For example, for CRTA data, an additional experiment such as a jumping CRTA[46] would be required for determining the E value.

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