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Kinetic Analysis of Solid-State Reactions: A General Empirical Kinetic Model

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In this research note, we presented a general empirical kinetic model that can fit any ideal kinetic model and even deviations produced by heterogeneities in particle shapes. The algebraic expression of the general empirical kinetic model is $f(\alpha) = \alpha^m(1 - q\alpha)^n$. The kinetic model can be used for performing the kinetic analysis of experimental data without previous assumptions about the form of the reaction kinetic model. The empirical kinetic model has been evaluated from the theoretical and experimental data.

1. Introduction

Under nonisothermal conditions, the reaction rate of a thermally stimulated solid-state reaction can be described by the following differential equation:¹

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (1)$$

where α is conversion degree, T is the temperature, R is the universal gas constant, A is the frequency factor, E is the activation energy, and $f(\alpha)$ is the kinetic model in differential form.

The value of the activation energy can be obtained from the multiple heating rate experimental data by means of a certain isoconversional method,² i.e., Friedman method,³ the nonlinear differential isoconversional method suggested by Budrugeac,⁴ Flynn–Wall–Ozawa method,^{5,6} Kissinger method,⁷ the linear integral isoconversional method suggested by Popescu,⁸ the nonlinear integral isoconversional method suggested by Vyazovkin,⁹ and its modification.¹⁰

Different mathematical forms for $f(\alpha)$ depending on the physical mechanisms assumed in the mathematical derivations have been proposed in the literature.¹¹ These mechanisms are proposed considering different geometrical assumptions for particle shapes and driving forces.^{12,13} The $f(\alpha)$ functions for the most extensively used mechanisms in solid-state reactions are included in Table 1. However, those ideal kinetic models cannot successfully describe some real solid-state processes due to heterogeneity in the solid reactants.^{14–16} Some deviations from the ideal kinetic models are expected, which imply a limitation in the kinetic analysis because none of the conventional kinetic models already proposed will properly fit all of the experimental data.¹⁴ To overcome this limitation, an alternative solution is the use of some empirical kinetic models. In the paper of Pérez-Maqueda et al.,¹⁴ a general fitting function for $f(\alpha)$ based on the Šesták–Berggren equation¹⁷ has been presented. On the basis of the empirical kinetic model suggested by Pérez-Maqueda et al.,¹⁴ a new general empirical kinetic model which can perfectly fit any of the ideal kinetic model has been presented. The corresponding equivalent equations for the conventional kinetic model are also obtained. Finally, the general empirical kinetic model presented in this research note is applied to the theoretical and experimental data.

2. Theory

As stated in the Introduction, those ideal kinetic models, although having successfully described many real solid-state reaction processes, might not be used for every process. To overcome this restriction, we proposed the use of the following expression for the $f(\alpha)$ function:

$$f(\alpha) = \alpha^m(1 - q\alpha)^n \quad (2)$$

The above equation is a modification of the empirical fitting function for $f(\alpha)$ suggested by Pérez-Maqueda et al.:¹⁴

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (3)$$

Equation (3) is a simplified form of the Šesták–Berggren equation:^{17,18}

$$f(\alpha) = (1 - \alpha)^n \alpha^m [-\ln(1 - \alpha)]^p \quad (4)$$

On the basis of the $f(\alpha)$ functions normalized at $\alpha = 0.5$, the resulting m , n , and q parameters have been calculated by fitting the different $f(\alpha)$ functions with eq 2; the corresponding equivalent functions describing the different ideal kinetic models are listed in Table 1. The plots of $f(\alpha)/f(0.5)$ versus α together with the equivalent functions with the corresponding m , n , and q parameters are presented in Figure 1. The residual errors involved in the equivalent functions deviating from the corresponding ideal kinetic models are also shown in Figure 1. It is quite evident that the fitting is excellent. Therefore, the general empirical kinetic model presented in this research note can describe every kinetic model listed in Table 1 just by selecting the proper m , n , and q parameters.

To compare the new empirical equation with the previously proposed one, the equivalent functions for A2, A3, D2, and D3 suggested by Pérez-Maqueda et al.¹⁴ are introduced (the expressions of those functions can be obtained from Table 1 in ref 14). The residual errors of the equivalent functions for A2, A3, D2, and D3 suggested by Pérez-Maqueda et al.¹⁴ deviating from the corresponding ideal kinetic models are shown in Figure 2. For comparison, the residual errors involved in the equivalent functions presented in this research note deviating from the corresponding ideal kinetic models are also illustrated in Figure 2. It is clear that the new empirical kinetic model provides a better fit of the corresponding ideal kinetic model than the empirical function suggested by Pérez-Maqueda et al.¹⁴

3. Results and Discussion

Some possible deviations from ideal model functions might be produced if particles in the material are not homogeneous

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Table 1. Algebraic Expressions for the $f(\alpha)$ Functions for the Most Common Mechanisms in Solid-State Reactions and Their Corresponding Equivalent General Empirical Kinetic Model

model	symbol	$f(\alpha)$	general empirical kinetic model $\alpha^m(1 - q\alpha)^n$		
			m	n	q
phased boundary controlled reaction	R2	$2(1 - \alpha)^{1/2}$	0	0.5	1
	R3	$3(1 - \alpha)^{2/3}$	0	2/3	1
nucleation and growth (Avrami–Erofeev)	A1.5	$\frac{3}{2}(1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$	0.337951	0.856039	1.002758
	A2	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	0.511148	0.793815	1.003138
	A2.5	$\frac{5}{2}(1 - \alpha)[- \ln(1 - \alpha)]^{3/5}$	0.616058	0.757249	1.003380
	A3	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	0.686443	0.733121	1.003553
	A4	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	0.775036	0.703294	1.003780
one-dimensional diffusion	D1	$\frac{2}{\alpha}$	−1	0	
two-dimensional diffusion	D2	$-\frac{1}{\ln(1 - \alpha)}$	−1.002367	0.507436	0.935544
three-dimensional diffusion (Jander)	D3	$\frac{3(1 - \alpha)^{2/3}}{2[1 - (1 - \alpha)^{1/3}]}$	−1.001978	1.001608	0.975270
three-dimensional diffusion (Ginstling–Brounshtein)	D4	$\frac{3(1 - \alpha)^{1/3}}{2[1 - (1 - \alpha)^{1/3}]}$	−1.002229	0.666892	0.963165
three-dimensional diffusion (Zhuravlev–Lesokin–Tempelman)	D5	$\frac{3(1 - \alpha)^{5/3}}{2[1 - (1 - \alpha)^{1/3}]}$	−1.001073	2.022097	0.981946
three-dimensional diffusion (Komatsu–Uemura)	D6	$\frac{3(1 + \alpha)^{2/3}}{2[(1 + \alpha)^{1/3} - 1]}$	−0.999639	1.109796	−0.894929
first-order reaction	F1	$(1 - \alpha)$	0	1	1
second-order reaction	F2	$(1 - \alpha)^2$	0	2	1
third-order reaction	F3	$(1 - \alpha)^3$	0	3	1
Prout–Tompkins	PT	$\alpha(1 - \alpha)$	1	1	1
reduced Šesták–Berggren function	RSB	$\alpha^m(1 - \alpha)^n$	m	n	1

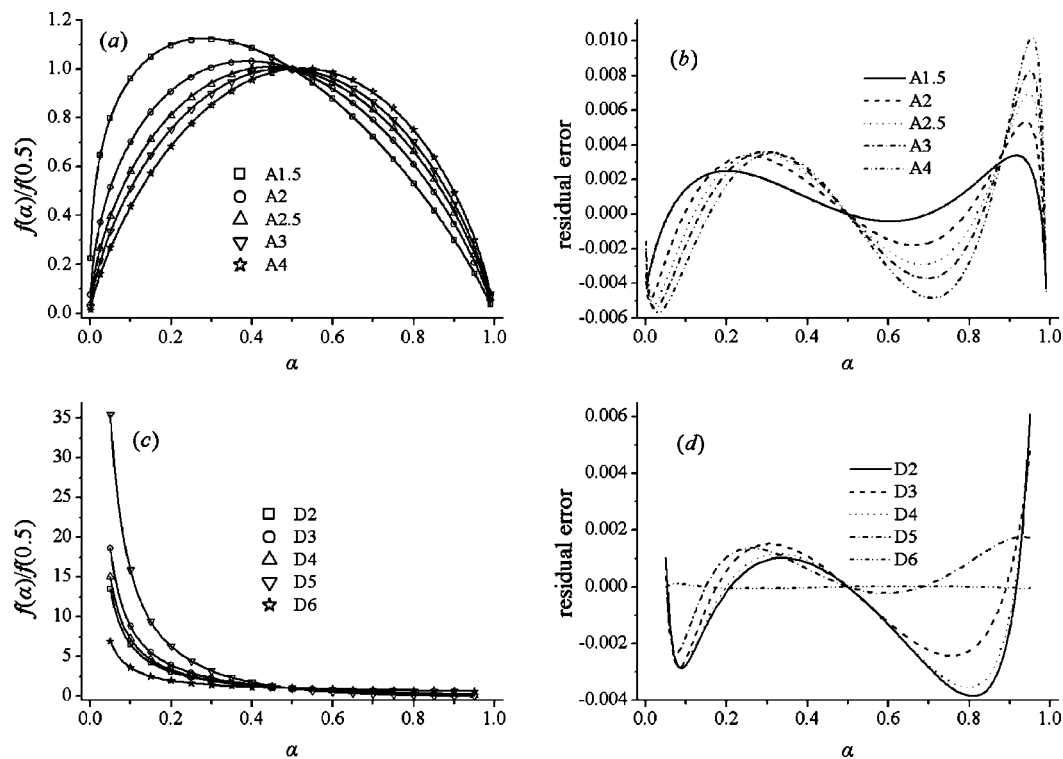


Figure 1. (a) Comparison of the $f(\alpha)$ functions corresponding to nucleation–growth mechanisms (dots) with the general kinetic models with the corresponding m , n , and q parameters tabulated in Table 1 (solid lines). (b) Residual errors of the equivalent functions deviating from the $f(\alpha)$ functions corresponding to nucleation–growth mechanisms. The residual error has been defined by the expression: $f_a(\alpha)/f_a(0.5) - f(\alpha)/f(\alpha)$, being $f_a(\alpha)$ the value obtained by the equivalent function and $f(\alpha)$ the value obtained by the ideal kinetic model. (c) Comparison of the $f(\alpha)$ functions corresponding to diffusion mechanisms (dots) with the general kinetic models with the corresponding m , n , and q parameters tabulated in Table 1 (solid lines). (d) Residual errors of the equivalent functions deviating from the $f(\alpha)$ functions corresponding to diffusion mechanisms.

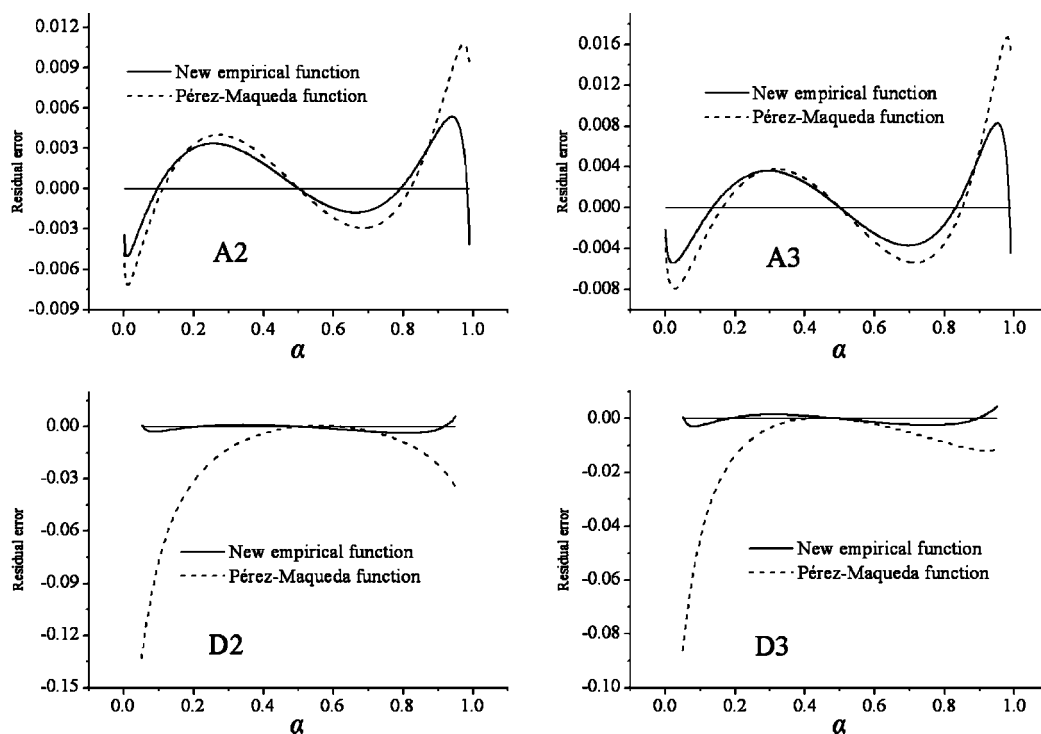


Figure 2. Comparison of the fitting of the ideal kinetic models provided by the empirical functions suggested by Pérez-Maqueda et al.¹⁷ and presented in this paper.

in shape. The nonisothermal simulated data have been analyzed. The nonisothermal data have been simulated by assuming that the sample is constituted by two different kinds of particles, i.e., spherical (50%) and cylindrical (50%), whose decompositions follow interface controlled kinetic models (R3 and R2,

respectively) with a unique activation energy ($E = 100 \text{ kJ mol}^{-1}$) and frequency factor ($A = 10^{10} \text{ min}^{-1}$). The Runge–Kutta method of fourth-order has been employed to integrate eq 1. Substitution of the obtained α – T data into eq 1 gives the reaction rate as a function of temperature.

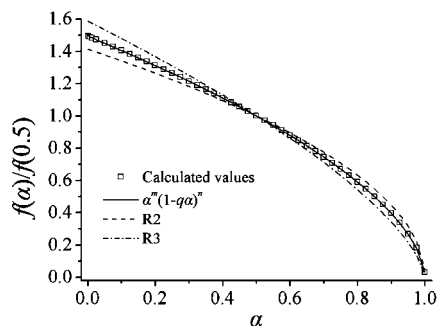


Figure 3. Overlay of the $f(\alpha)/f(0.5)$ values calculated by the master plot method and by the general empirical kinetic model with the resulting values of m , n , and q , i.e., $m = -7.7265 \times 10^{-4}$, $n = 0.576\,805$, and $q = 0.999\,641$. Ideal kinetic models R3 and R2 are also plotted.

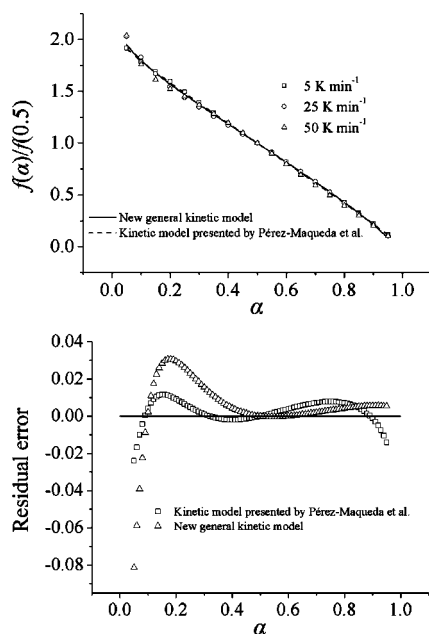


Figure 4. Overlay of the experimental values of $f(\alpha)/f(0.5)$ (dots) and the values of $f(\alpha)/f(0.5)$ (line) calculated by kinetic models presented in this paper and in the paper of Pérez-Maqueda et al.¹⁷

The activation energy value of this simulated process can be obtained by means of the Friedman method.³ The obtained value of the activation energy is coincident with that used for the simulation. Then, the values of $f(\alpha)/f(0.5)$ versus α can be obtained by the master plot method.^{19,20} Using as reference point $\alpha = 0.5$, the following equation is easily derived from eq 1

$$\frac{f(\alpha)}{f(0.5)} = \frac{(d\alpha/dT)_\alpha e^{E/RT_\alpha}}{(d\alpha/dT)_{0.5} e^{E/RT_{0.5}}} \quad (5)$$

where the subscript α denotes the values related to a given degree of conversion, $(d\alpha/dT)_{0.5}$, and $T_{0.5}$ are the values of $(d\alpha/dT)$ and T at $\alpha = 0.5$, respectively.

The resulting values of $f(\alpha)/f(0.5)$ versus α are shown in Figure 3. The normalized general empirical kinetic model with resulting values of m , n , and q is also represented in Figure 3 as a function of α together with the $f(\alpha)/f(0.5)$ functions for R3 and R2. It can be observed that the general empirical kinetic model perfectly describes the real kinetic model of this simulated process by selecting the proper m , n , and q parameters.

Once the method has been illustrated from the theoretical data, it is of interest to verify it with the experimental data. Thus, the nonisothermal kinetics of cellulose pyrolysis has been

analyzed. The kinetic conversion data of cellulose pyrolysis was obtained from the literature.²¹ The experiment was performed under nonisothermal conditions at three heating rates of 5, 25, and 50 K min⁻¹, and a purge of nitrogen with a flow rate of 60 mL min⁻¹.

The activation energy of cellulose pyrolysis has been determined by the stationary point method.²² The value of E is established: $E = 218.43 (\pm 3.35)$ kJ mol⁻¹. By virtue of eq 5 and $E = 218.43$ kJ mol⁻¹, the experimental values of $f(\alpha)/f(0.5)$ versus α can be calculated. As shown in Figure 4, for all the heating rates, the curves of $f(\alpha)/f(0.5)$ versus α exhibit the same shape, with very low differences among the $f(\alpha)/f(0.5)$ values for a given α . The scattering noted in Figure 4 is due to the standard deviation of the activation energy. The corresponding values of $f(\alpha)/f(0.5)$ versus α calculated by the proposed general empirical kinetic model and the kinetic model presented by Pérez-Maqueda et al.¹⁴ It can be observed that the new empirical function perfectly matches the real kinetic model.

4. Conclusions

It has been shown that the general empirical kinetic model presented in this research note fits all of the equations corresponding to ideal kinetic models. The proposed empirical kinetic model has been proved to be quite useful for analyzing not only data that fit any of ideal kinetic models commonly used in the literature but also processes that cannot be described by one of those ideal models. The general function presented in this research note has been verified with both theoretical and experimental data. Thus, a set of curves at different heating rates simulated by assuming that the sample is constituted by two different kinds of particles, whose decompositions follow R3 and R2, have been analyzed. Additionally, the kinetic data of cellulose pyrolysis at different heating rates have been studied.

Acknowledgment

This research was financed by National Natural Science Foundation of China (Project No. 50806048).

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Received for review December 3, 2008

Revised manuscript received February 5, 2009

Accepted February 11, 2009

IE8018615