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Model Dependence of the Activation Energy Derived from Nonisothermal Kinetic Data

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This work intends to explain mathematically the model dependence of the activation energy, E_a, derived from fitting nonisothermal kinetic data to a kinetic model. Artificial data following single reaction mechanisms, both isothermal and nonisothermal, were generated to fit exactly the following simulated kinetic models: first-order reaction, fourth-order Avrami−Erofeyev process, and one-dimensional diffusion. To simulate more closely experimental data, random errors, corresponding to $\pm 0.1\%$ of the maximum conversion value, were embedded in the data by adding a random number bounded by ± 0.001 to each data point. For isothermal data, any kinetic model leads to the correct value of E_a. However, for nonisothermal data, the calculated E_a deviates from the correct value by an amount, ΔE_a, that depends strongly on the kinetic model to which the data are fit. In addition, the apparent frequency factor depends slightly on the kinetic model for isothermal data, but depends strongly on the model for nonisothermal data. The results highlight the severe limitations of fitting nonisothermal data to kinetic models.

Introduction

Kinetic analyses of solid-state reactions are usually performed by the model-fitting approach, in which the kinetic data are fitted to a variety of kinetic equations in the following form:

$$\mathrm{d}x/\mathrm{d}t = k(T)\,\mathrm{f}(x) = A\exp(-E_a/RT)\,\mathrm{f}(x) \qquad (1)$$

where x is the fraction of reactant converted ($0 \le x \le 1$), t is the time, and $k(T)$ is the rate constant that depends only on the absolute temperature, T, the activation energy, E_a, and the frequency factor, A. The term $\mathrm{f}(x)$ represents the specific reaction model (Table 9), and is sometimes also called the differential conversion function or the differential kinetic function.[1,2] The three kinetic parameters, E_a, A, and $\mathrm{f}(x)$, are considered to be crucial to kinetic studies and are sometimes referred to as the "kinetic triplet", and are usually not separable. The aim of kinetic studies is to extrapolate this kinetic triplet, which can be useful for mechanistic interpretation and kinetic prediction. In the model-fitting approach, this goal is achieved by fitting various reaction models to the kinetic data and determining the model of best fit, on the basis of statistical arguments, namely, the determination coefficient, R^2, and the randomness of the residuals. After the model of best fit has been determined, the activation energy and frequency factor can then be calculated. More often, the integral version of eq 1 is used to reduce the noise of the differential data:[3]

$$\mathrm{g}(x) = \int_0^x \frac{\mathrm{d}x}{\mathrm{f}(x)} = \int_0^t k(T)\,\mathrm{d}t = \int_0^t A\exp(-E_a/RT)\,\mathrm{d}t \qquad (2)$$

where $\mathrm{g}(x)$ is termed the integral kinetic function that represents various reaction models (Table 9). In nonisothermal studies, approximations have been applied to the integral in various forms[4−9] to linearize eq 2. For example, the Coats−Redfern[5] approximation has the following form:

$$\ln[g(x)/T^2] = \ln[(AR/qE_a)(1 - 2RT/E_a)] - E_a/RT \qquad (3)$$

where q is the linear heating rate in degrees Celsius per minute.

However, in isothermal studies, the activation energies obtained by fitting the data to different models are often found to be identical.[2,10] In other words, model-fitting of isothermal data will always afford a consistent activation energy regardless of the reaction model fitted. On the other hand, in nonisothermal studies, the activation energy differs significantly among different fitted models, such that the kinetic parameters of the reaction appear ambiguous.[3,11,12] The nonisothermal Arrhenius parameters often disagree with the isothermal values, even when only a single reaction mechanism is involved. Possible reasons are that Arrhenius parameters are highly model-dependent and that the reaction model may not have been determined correctly. Application of the model-fitting approach to nonisothermal kinetic data has raised concerns. Generally, the agreement between the results obtained from isothermal and nonisothermal data is poor unless the correct model is used. This disagreement has led some authors to conclude that nonisothermal data are not meaningful.[13] However, this point of view has been seriously challenged.[6]

The model independence of the isothermal activation energy and the model dependence of the nonisothermal activation energy have not yet been explained.[2] In this article, we wish to present our understanding of, and hence to explain, these phenomena in model-fitting. First, a general mathematical treatment to model-fitting analysis is presented. Second, the mathematically derived conclusions are scrutinized by analyzing the simulated data. Real experimental data were not used because the inherent experimental errors might lead to spurious conclusions. Furthermore, the true mechanistic conclusions cannot be guaranteed for real experimental data.

Mathematical Analysis of Model-Fitting. The following provides a general analysis to the activation energy, E_a, and

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the frequency factor, A, obtained from fitting various reaction models to solid-state kinetic data. Because no particular mechanistic or mathematical kinetic model is assumed, the conclusion should be generally valid.

Activation Energy. According to eq 1, the activation energy for an arbitrary reaction model, $f(x)$, fitted to the differential data, can be obtained from:

$$\begin{aligned} E_a &= -R\frac{d\ln[(dx/dt)/f(x)]}{d(1/T)} \\ &= -R\frac{d\ln[(dx/dt)/f^0(x)]}{d(1/T)} + R\frac{d\ln[f'(x)]}{d(1/T)} \\ &= E_a{}^0 + \Delta E_a \end{aligned} \qquad (4)$$

where $f^0(x)$ is the exact reaction model, which can be ascertained only with simulated data, while $f'(x) = f(x)/f^0(x)$ is the "correction term" of the fitted model with respect to the exact model by assuming $f(x) = f^0(x)\,f'(x)$. Therefore, the apparent activation energy for any fitted model consists of two terms, the true activation energy, $E_a{}^0$, and the activation energy correction, ΔE_a, where $\Delta E_a = R\, d\ln[f'(x)]/d(1/T)$, which depends only on the above correction term of the fitted model.

Alternatively, model fitting can be performed on the integral kinetic data utilizing eq 2. Under a linear heating rate and applying the Coats−Redfern approximation,[5] eq 2 can be simplified. The fitted apparent E_a can be calculated as:

$$\begin{aligned} E_a &= -R\frac{d\ln[g(x)/T^2]}{d(1/T)} \\ &= -R\frac{d\ln[g^0(x)/T^2]}{d(1/T)} - R\frac{d\ln[g'(x)]}{d(1/T)} \\ &= E_a{}^0 + \Delta E_a \end{aligned} \qquad (5)$$

where $g^0(x)$ is the exact model, while $g'(x) = g(x)/g^0(x)$ is the correction term of the fitted integral model with respect to the exact model and $\Delta E_a = -R\, d\ln[g'(x)]/d(1/T)$ is the correction term. When the integral model is fitted to isothermal data, exactly the same ΔE_a term is obtained, and therefore eq 5 is valid for fitting of both isothermal and nonisothermal data to the integral models.

Combining the above considerations, no matter whether the differential form or the integral form is used, the fitted activation energy, E_a, is equal to the true activation energy, $E_a{}^0$, plus the correction term, ΔE_a.

The derived correction terms of the various models in Table 9, with respect to the first-order model (F1), the fourth-order Avrami−Erofeyev model (A4), and the one-dimensional diffusion model (D1), are shown in Tables 10−12, respectively. Because $f'(x)$ and $g'(x)$ are mathematical functions that have a unique form for a given model, or more exactly, because $f'(x)$ and $g'(x)$ have a different temperature dependence, fitting of data to the differential form of a given model generally will not give the same E_a as fitting to the integral form of the same model.

Equations 4 and 5 show how different situations arise from model-fitting of isothermal and nonisothermal data. Because $E_a = E_a{}^0 + \Delta E_a$, model-fitting will give the correct activation energy only when $\Delta E_a = 0$; otherwise model-dependent activation energy is expected.

In isothermal studies, because each experiment is performed at the same temperature, the kinetic data, x, will not show temperature dependence other than that predicted by the Arrhenius equation. Therefore, $f'(x)$ and $g'(x)$ have no apparent additional temperature dependence, and thus $\Delta E_a = 0$. In other words, no matter which model is used to fit the isothermal kinetic data, the correct E_a is always obtained. A similar conclusion is not reached for the frequency factor, A, as will be shown later. However, this conclusion is valid only for reactions with a single mechanism. For reactions that have complicated mechanisms, the conclusion does not hold. Unfortunately, many solid-state reactions are complicated, usually involving multiple steps. The complexity of a solid-state reaction can be readily detected by the model-free (or isoconversional) method,[14] an alternative kinetic approach to the model-fitting method. The purpose of this article, however, is not to explain how to determine the correct kinetic parameters, especially for those complicated solid-state reactions, but rather to explain certain published kinetic data.

On the other hand, in nonisothermal studies, the temperature is arranged to change appreciably. The fractional conversion, x, depends on the reaction mechanism (usually represented by a kinetic model, as in Table 9), the time, t, and the temperature, T. As a result, the kinetic information is convoluted with the temperature regime so that x is forced to depend on the temperature regime besides that determined by the Arrhenius equation. Therefore, unless the correct model is used, $\Delta E_a \neq 0$ for model-fitting of nonisothermal data, and thus different models of fitting lead to different apparent activation energies. The true E_a will not be obtained for nonisothermal data unless the correct model is selected. The condition, $f(x) = \text{constant}\cdot f^0(x)$, leads to the same E_a value.

Frequency Factor. The frequency term, $\ln A$, is also obtained from model fitting. Rearranging eq 1, $\ln A$ can be obtained from fitting to the differential kinetic data. Thus:

$$\begin{aligned} \ln A &= \ln[(dx/dt)/f(x)] + E_a/RT \\ &= \{\ln[(dx/dt)/f^0(x)] + E_a{}^0/RT\} + \\ &\qquad \{-\ln[f'(x)] + \Delta E_a/RT\} \\ &= \ln A^0 + \Delta\ln A \end{aligned} \qquad (6)$$

where A^0 is the true frequency factor. Similarly, when fitting to the integral data:

$$\begin{aligned} \ln A &= \ln A^0 + \{\ln[g'(x)] + \Delta E_a/RT\} \\ &= \ln A^0 + \Delta\ln A \end{aligned} \qquad (7)$$

By analogy with the final line of eq 5, $\ln A$ also consists of two components: the true $\ln A^0$ and the correction term, $\Delta\ln A$.

In isothermal studies, $\Delta E_a = 0$. However, $\ln A = \ln A^0 - \ln[f'(x)]$ for fitting of the isothermal kinetic data to the differential form, or $\ln A = \ln A^0 + \ln[g'(x)]$ for fitting the same data to the integral form. Therefore, although the correct E_a is obtained from isothermal data regardless of the model fitted, the fitted frequency factor, $\ln A$, is slightly model-dependent. In nonisothermal studies, $\Delta E_a \neq 0$, and therefore, $\ln A$ depends not only on $\ln[f'(x)]$ or $\ln[g'(x)]$, but especially on the correction term, ΔE_a. Because ΔE_a is strongly model-dependent, $\ln A$ will also be strongly dependent on the fitted model. As a consequence, both the apparent E_a and $\ln A$ are model-dependent for nonisothermal data.

The results of the above analysis do not depend on the origin of the simulated data. Hence, the results should be generally applicable to kinetic data from all sources, corresponding to any mechanistic or mathematical kinetic model.

Data Simulation and Analysis. Three solid-state processes, a first-order process (F1), a fourth-order Avrami−Erofeyev process (A4), and a one-dimensional diffusion process (D1), were simulated under isothermal and nonisothermal conditions. The kinetic parameters were assumed to be the same in all three cases: $E_a = 167.2$ kJ/mol and $A = 10^{19}$ min^{-1}. These models were chosen because they are frequently encountered in many solid-state reactions. The first-order reaction is a simple model that approximates many degradation processes.[15,16] The Avrami−Erofeyev[17−21] model usually describes the crystallization kinetics from amorphous phases,[10,22,23] as well as that of many processes involving nucleation and growth of nuclei. The so-called square-root time relationship is an example of one-dimensional diffusion.[24] However, a similar relationship can be derived from the KWW equation that describes the molecular dynamics of amorphous materials,[25] whose chemical and physical stabilities, including protein aggregation and crystallization,[26] proceed according to the time raised to the power of β, which is a constant that describes the dynamics of the amorphous material.

The first-order process (F1) was simulated isothermally at 140, 150, 160, and 170 °C and nonisothermally at heating rates of 8, 12, 16 °C/min, using eq 2. Under isothermal conditions, eq 2, when applied to the first-order model, is relatively simple, and the fractional conversion can be calculated as:

$$x = 1 - \exp[-k(T)t] \tag{8}$$

Under a linear heating rate of q °C/min, eq 2 can be transformed as:

$$x = 1 - \exp[-(A/q)\int_0^T \exp(-E_a/RT)\,\mathrm{d}T] \tag{9}$$

The integral in the exponential can be accurately evaluated using the Senum−Yang approximation,[27] as follows, where $z = E_a/RT$:

$$\int_0^z z^2 \exp(-z)\,\mathrm{d}z = \frac{\exp(-z)}{z}\,\frac{z^2 + 10z + 18}{z^3 + 12z^2 + 36z + 24} \tag{10}$$

In all cases, the data are generated in equal intervals of time. Differentiation of the kinetic data was performed employing the centered difference approximation:[28]

$$(\mathrm{d}x/\mathrm{d}t)_i = (x_{i+1} - x_{i-1})/2\Delta t \tag{11}$$

where the subscript i denotes the ith data point and Δt is the time interval between the adjacent data points. Because a large number of data points (2000−4000) are generated, differentiation does not lead to significant noise, as can be seen from the small standard deviations of the fitted parameters to the simulated data.

The fourth-order Avrami−Erofeyev kinetics (A4) were simulated under the same conditions as in the simulated first-order process. The fractional conversions under isothermal conditions and nonisothermal conditions were calculated according to eqs 12 and 13, respectively.

$$x = 1 - \exp[-(kt)^4] \tag{12}$$

$$x = 1 - \exp\{-[(A/q)\int_0^T \exp(-E_a/RT)\,\mathrm{d}T]^4\} \tag{13}$$

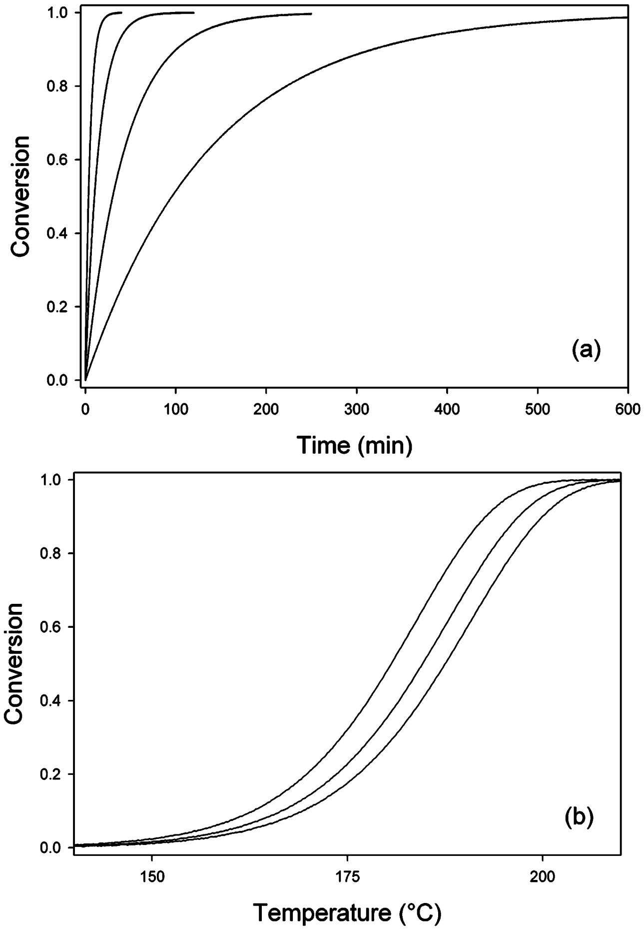

Figure 1. Simulated first-order process (F1) with Arrhenius parameters, $E_a = 167.2$ kJ/mol and log(A*min) = 19, under (a) isothermal conditions (170, 160, 150, and 140 °C from left to right) and (b) nonisothermal conditions (heating rates of 8, 12, 16 °C/min from left to right).

TABLE 1: Activation Energy, E_a, and the Common Logarithm of the Frequency Factor, log A, Obtained from Fitting of the Simulated First-Order Kinetic Data (from x = 0.01 to x = 0.99) under Isothermal Conditions (shown in Figure 1a) to a Range of Kinetic Functions, Corresponding to Various Models

model	E_a (kJ/mol)	log (A*min)	R^2
A2	167.2 ± 0.1	18.57 ± 0.01	1.000
A3	167.2 ± 0.2	18.37 ± 0.02	1.000
A4	167.2 ± 0.2	18.23 ± 0.02	1.000
D1	167.3 ± 0.2	18.35 ± 0.02	1.000
D2	167.3 ± 0.1	18.36 ± 0.01	1.000
D3	167.2 ± 0.0	18.17 ± 0.00	1.000
D4	167.3 ± 0.1	17.86 ± 0.01	1.000
F1[a]	167.2 ± 0.0	19.00 ± 0.00	1.000
F2	167.1 ± 0.3	20.20 ± 0.04	1.000
P1	167.2 ± 0.1	19.12 ± 0.02	1.000
PL2	167.3 ± 0.3	18.04 ± 0.04	1.000
PL3	167.2 ± 0.4	17.91 ± 0.05	1.000
PL4	167.2 ± 0.4	17.81 ± 0.05	1.000
R1	167.3 ± 0.2	18.22 ± 0.03	1.000
R2	167.3 ± 0.1	18.26 ± 0.02	1.000
R3	167.3 ± 0.1	18.22 ± 0.01	1.000

[a] This model corresponds exactly to the simulated data.

Again, the integral in the exponential was evaluated using the Senum−Yang approximation.[27]

The one-dimensional diffusion kinetics (D1) were simulated under isothermal conditions (140, 150, and 160 °C) and nonisothermal (8, 12, and 16 °C/min) conditions. The fractional

TABLE 2: Activation Energy, E_a, and the Common Logarithm of the Frequency Factor, log *A*, Obtained from Fitting of the Simulated First-Order Nonisothermal (12 °C/min) Kinetic Data (from $x = 0.01$ to $x = 0.99$) to Differential Kinetic Functions, f(x), Corresponding to Various Models

model	$E_a{}^a$	log(A*min)	R^2	$\Delta E_a{}^a$	$E_a = E_a{}^0 + \Delta E_a$
A2	79.8 ± 0.2	8.80 ± 0.02	0.999	−87.3	79.9
A3	50.7 ± 0.2	5.33 ± 0.02	0.996	−116.4	50.8
A4	36.1 ± 0.2	3.56 ± 0.02	0.992	−130.9	36.3
D1	217.1 ± 4.9	24.01 ± 0.57	0.872	50.0	217.2
D2	252.0 ± 3.7	27.94 ± 0.43	0.942	85.0	252.2
D3	298.0 ± 1.8	32.83 ± 0.21	0.990	131.0	298.2
D4	268.1 ± 3.0	29.23 ± 0.35	0.965	101.1	268.3
F1[b]	167.0 ± 0.2	18.98 ± 0.02	1.000	0	167.2
F2	256.6 ± 3.7	29.79 ± 0.43	0.943	89.6	256.8
P1	27.4 ± 1.2	3.45 ± 0.15	0.627	−139.6	27.6
PL2	7.7 ± 3.1	0.11 ± 0.36	0.021	−159.4	7.6
PL3	-15.6 ± 2.9	-2.66 ± 0.34	0.092	−182.7	−15.5
PL4	-27.2 ± 2.8	-4.08 ± 0.32	0.250	−194.3	−27.1
R1	77.5 ± 3.7	8.18 ± 0.43	0.605	−89.6	77.6
R2	122.3 ± 1.8	13.28 ± 0.22	0.938	−44.8	122.4
R3	137.2 ± 1.2	14.90 ± 0.14	0.977	−29.9	137.3

[a] In kilojoules per mole. [b] This model corresponds exactly to the simulated data.

TABLE 3: Activation Energy, E_a, and the Common Logarithm of the Frequency Factor, log *A*, Obtained from Fitting of the Simulated First-Order Nonisothermal (12 °C/min) Kinetic Data (from $x = 0.01$ to $x = 0.99$) to Integral Kinetic Functions, g(x), Corresponding to Various Models

model	$E_a{}^a$	log(A*min)	R^2	$\Delta E_a{}^a$	$E_a = E_a{}^0 + \Delta E_a$
A2	79.8 ± 0.0	8.81 ± 0.01	1.000	−87.3	79.9
A3	50.8 ± 0.0	5.35 ± 0.00	1.000	−116.4	50.8
A4	36.2 ± 0.0	3.59 ± 0.00	1.000	−130.9	36.3
D1	271.8 ± 2.5	30.51 ± 0.29	0.977	104.6	271.8
D2	289.7 ± 2.0	32.41 ± 0.23	0.987	122.6	289.8
D3	314.2 ± 1.1	34.74 ± 0.13	0.996	147.1	314.3
D4	297.7 ± 1.7	32.73 ± 0.20	0.991	130.5	297.7
F1[b]	167.1 ± 0.1	18.99 ± 0.01	1.000	0	167.2
F2	221.7 ± 2.5	25.69 ± 0.29	0.965	54.6	221.8
P1[c]	24.1 ± 0.1	3.06 ± 0.01	0.993	—[c]	—[c]
PL2	62.4 ± 0.6	6.61 ± 0.07	0.972	−104.8	62.4
PL3	39.1 ± 0.4	3.85 ± 0.05	0.968	−128.0	39.2
PL4	27.5 ± 0.3	2.45 ± 0.04	0.964	−139.7	27.5
R1	132.2 ± 1.2	14.67 ± 0.14	0.975	−35.0	132.2
R2	147.3 ± 0.8	16.25 ± 0.09	0.992	−19.8	147.4
R3	153.4 ± 0.6	16.82 ± 0.06	0.996	−13.8	153.4

[a] In kilojoules per mole. [b] This model corresponds exactly to the simulated data. [c] The activation energy in the table is obtained by an iterative process. Fitting of the kinetic function for P1 (Prout−Tompkins) to nonisothermal kinetic data is more complicated, because the model includes a term, $t_{1/2}$, which depends on the fitted E_a itself. Hence, the correction term, ΔE_a, cannot be obtained for this kinetic function.

conversions under isothermal conditions and nonisothermal conditions were calculated according to eqs 14 and 15, respectively.

$$x = \sqrt{kt} \tag{14}$$

$$x = [(A/q)\int_0^T \exp(-E_a/RT)\, dT]^{1/2} \tag{15}$$

TABLE 4: Activation Energy, E_a, and the Common Logarithm of the Frequency Factor, log *A*, Obtained from Fitting of the Simulated Fourth-Order Avrami−Erofeyev Kinetic Data (from $x = 0.01$ to $x = 0.99$) under Isothermal Conditions (shown in Figure 2a) to a Range of Kinetic Functions, Corresponding to Various Models

model	E_a (kJ/mol)	log(A*min)	R^2
A2	167.3 ± 0.1	19.26 ± 0.01	1.000
A3	167.2 ± 0.0	19.11 ± 0.00	1.000
A4[a]	167.2 ± 0.0	19.00 ± 0.00	1.000
D1	167.3 ± 0.0	19.03 ± 0.00	1.000
D2	167.3 ± 0.1	18.98 ± 0.01	1.000
D3	167.5 ± 0.3	18.71 ± 0.04	1.000
D4	167.4 ± 0.1	18.45 ± 0.02	1.000
F1	167.5 ± 0.3	19.58 ± 0.03	1.000
F2	168.3 ± 1.4	20.67 ± 0.17	1.000
P1	167.2 ± 0.1	19.86 ± 0.01	1.000
PL2	167.1 ± 0.1	18.94 ± 0.01	1.000
PL3	167.1 ± 0.1	18.85 ± 0.02	1.000
PL4	167.1 ± 0.1	18.77 ± 0.02	1.000
R1	167.2 ± 0.1	19.02 ± 0.01	1.000
R2	167.3 ± 0.0	18.95 ± 0.00	1.000
R3	167.3 ± 0.1	19.26 ± 0.01	1.000

[a] This model corresponds exactly to the simulated data.

TABLE 5: Activation Energy, E_a, and the Common Logarithm of the Frequency Factor, log *A*, Obtained from Fitting of the Simulated Fourth-Order Nonisothermal (12 °C/min) Avrami−Erofeyev Kinetic Data (from $x = 0.01$ to $x = 0.99$) to Integral Kinetic Functions, g(x), Corresponding to Various Models

model	$E_a{}^a$	log(A*min)	R^2	$\Delta E_a{}^a$	$E_a = E_a{}^0 + \Delta E_a$
A2	341.8 ± 0.2	39.07 ± 0.02	1.000	174.7	341.9
A3	225.3 ± 0.1	25.71 ± 0.01	1.000	58.2	225.4
A4[b]	167.1 ± 0.1	18.99 ± 0.01	1.000	0	167.2
D1	1116.1 ± 9.7	126.69 ± 1.11	0.979	947.0	1114.2
D2	1186.6 ± 7.7	134.54 ± 0.88	0.988	1019.5	1186.7
D3	1282.3 ± 4.3	144.93 ± 0.49	0.997	1115.0	1282.2
D4	1217.6 ± 6.7	137.47 ± 0.76	0.991	1050.5	1217.7
F1	691.2 ± 0.4	78.92 ± 0.04	1.000	524.1	691.3
F2	904.9 ± 9.9	103.62 ± 1.13	0.967	736.8	904.0
P1[c]	115.2 ± 0.5	13.94 ± 0.05	0.995	—[c]	—[c]
PL2	273.3 ± 2.4	31.09 ± 0.28	0.977	105.7	272.9
PL3	179.7 ± 1.6	20.35 ± 0.18	0.976	12.2	179.4
PL4	132.8 ± 1.2	14.95 ± 0.14	0.978	−34.5	132.7
R1	554.2 ± 4.9	63.05 ± 0.55	0.993	386.1	553.3
R2	613.7 ± 3.0	69.65 ± 0.34	0.997	446.6	613.8
R3	637.3 ± 2.2	72.21 ± 0.25	1.000	470.1	637.3

[a] In kilojoules per mole. [b] This model corresponds exactly to the simulated data. [c] The activation energy in the table is obtained by an iterative process. Fitting of the kinetic function for P1 (Prout−Tompkins) to nonisothermal kinetic data is more complicated, because the model includes a term, $t_{1/2}$, which depends on the fitted E_a itself. Hence, the correction term, ΔE_a, cannot be obtained for this kinetic function.

A random number bounded by ±0.001, corresponding to noise at the level of ±0.1% of the maximum value, $\alpha = 1$, was added to every simulated data point to simulate more closely the experimental data. All these kinetic data in the range of $x = 0.01-0.99$ were fitted to various models according to the integral kinetic eq 2 to evaluate the model-independence and/or model-dependence of the kinetic parameters, E_a, and A. For isothermal data, eq 2 becomes:

$$g(x) = A \exp(-E_a/RT_{iso})t \tag{16}$$

where T_{iso} is the isothermal temperature. Under a linear heating rate, q °C/min, eq 2 can be linearized using the Coats−Redfern approximation,[5] shown in eq 3.

The differential kinetic eq 1 was also used to fit the first-order nonisothermal data to compare the differential and integral forms in model-fitting.

TABLE 6: Activation Energy, E_a, and the Common Logarithm of the Frequency Factor, log A, Obtained from Fitting of the Simulated One-Dimensional Diffusion Kinetic Data (from $x = 0.01$ to $x = 0.99$) under Isothermal Conditions (shown in Figure 3a) to a Range of Kinetic Functions, Corresponding to Various Models

model	E_a (kJ/mol)	log(A*min)	R^2
A2	167.1 ± 0.1	19.13 ± 0.01	1.000
A3	167.1 ± 0.1	18.95 ± 0.01	1.000
A4	167.2 ± 0.1	18.82 ± 0.01	1.000
D1[a]	167.2 ± 0.0	19.00 ± 0.00	1.000
D2	167.2 ± 0.0	18.96 ± 0.00	1.000
D3	167.0 ± 0.2	18.65 ± 0.02	1.000
D4	167.1 ± 0.1	18.41 ± 0.01	1.000
F1	167.0 ± 0.2	19.48 ± 0.02	1.000
F2	166.1 ± 1.2	20.28 ± 0.14	1.000
P1	167.1 ± 0.1	19.66 ± 0.01	1.000
PL2	167.2 ± 0.0	18.74 ± 0.00	1.000
PL3	167.2 ± 0.0	18.61 ± 0.00	1.000
PL4	167.2 ± 0.0	18.51 ± 0.00	1.000
R1	167.2 ± 0.0	18.91 ± 0.00	1.000
R2	167.2 ± 0.0	18.87 ± 0.00	1.000
R3	167.1 ± 0.1	18.79 ± 0.01	1.000

[a] This model corresponds exactly to the simulated data.

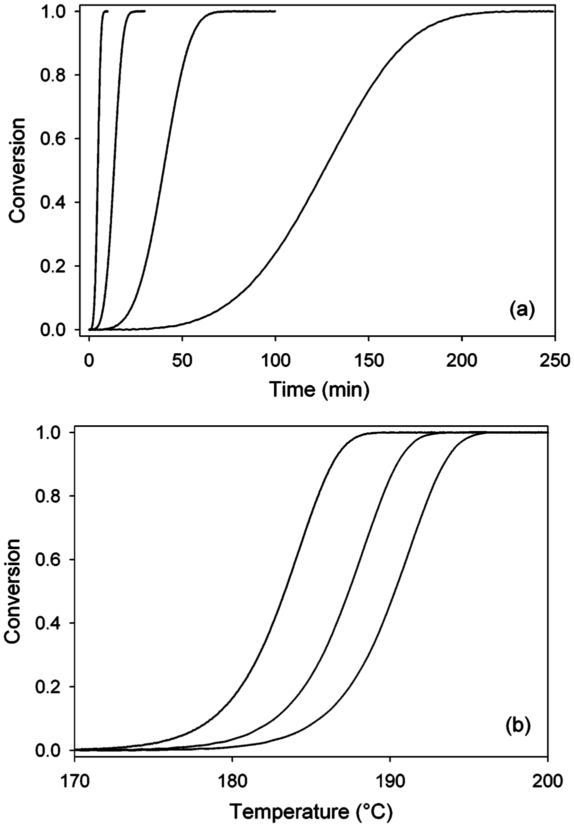

Figure 2. Simulated fourth-order Avrami−Erofeyev kinetic process (A4) with Arrhenius parameters, $E_a = 167.2$ kJ/mol and log(A*min) = 19, under (a) isothermal conditions (170, 160, 150, and 140 °C from left to right) and (b) nonisothermal conditions (heating rates of 8, 12, 16 °C/min from left to right).

TABLE 7: Activation Energy, E_a, and the Common Logarithm of the Frequency Factor, log A, Obtained from Fitting of the Simulated Nonisothermal (12 °C/min) One-Dimensional Diffusion Kinetic Data (from $x = 0.01$ to $x = 0.99$) to Integral Kinetic Functions, g(x), Corresponding to Various Models

model	E_a[a]	log(A*min)	R^2	ΔE_a[a]	$E_a = E_a^0 + \Delta E_a$
A2	42.7 ± 0.3	4.47 ± 0.03	0.985	−124.3	42.9
A3	26.1 ± 0.2	2.41 ± 0.02	0.982	−140.9	26.3
A4	17.8 ± 0.1	1.37 ± 0.02	0.979	−149.1	18.1
D1[b]	167.0 ± 0.1	18.97 ± 0.02	1.000	0	167.2
D2	174.0 ± 0.3	19.61 ± 0.04	0.999	7.1	174.3
D3	182.5 ± 0.7	20.08 ± 0.08	0.995	15.5	182.7
D4	176.8 ± 0.4	19.32 ± 0.05	0.998	9.8	177.0
F1	92.3 ± 0.5	10.49 ± 0.07	0.987	−74.7	92.5
F2	108.6 ± 1.5	12.67 ± 0.18	0.935	−58.4	108.8
P1[c]	17.7 ± 0.1	2.24 ± 0.17	0.979	—[c]	—[c]
PL2	36.5 ± 0.0	3.62 ± 0.00	1.000	−130.5	36.7
PL3	22.0 ± 0.0	1.83 ± 0.00	1.000	−145.0	22.2
PL4	14.8 ± 0.0	0.95 ± 0.00	0.999	−152.2	15.0
R1	80.0 ± 0.1	8.83 ± 0.01	1.000	−87.0	80.2
R2	85.7 ± 0.2	9.29 ± 0.03	0.997	−81.3	85.9
R3	87.8 ± 0.3	9.40 ± 0.04	0.995	−79.2	88.0

[a] In kilojoules per mole. [b] This model corresponds exactly to the simulated data. [c] The activation energy in the table is obtained by an iterative process. Fitting of the kinetic function for P1 (Prout−Tompkins) to nonisothermal kinetic data is more complicated, because the model includes a term, $t_{1/2}$, which depends on the fitted E_a itself. Hence, the correction term, ΔE_a, cannot be obtained for this kinetic function.

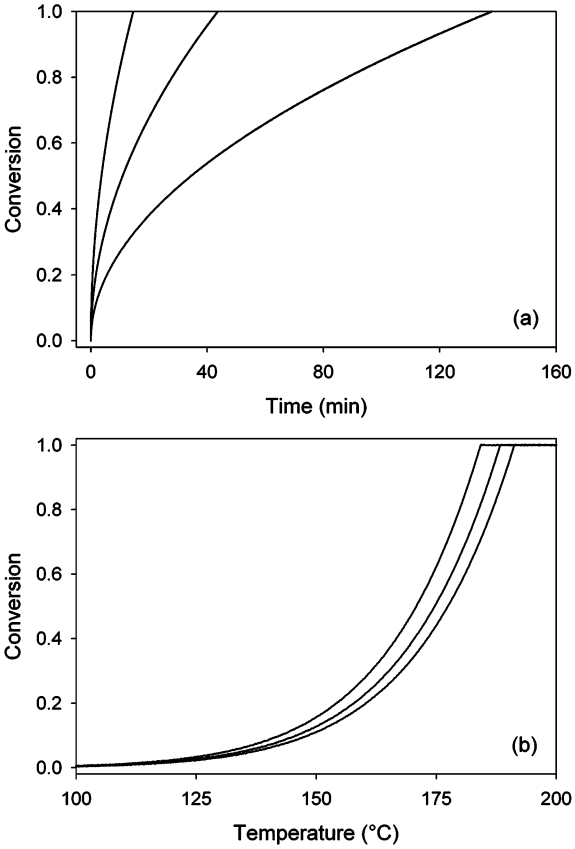

Figure 3. Simulated one-dimensional diffusion kinetic process (D1) with Arrhenius parameters, $E_a = 167.2$ kJ/mol and log(A*min) = 19, under (a) isothermal conditions (160, 150, and 140 °C from left to right) and (b) nonisothermal conditions (heating rates of 8, 12, 16 °C/min from left to right).

Results and Discussion

Figure 1a shows the simulated first-order data under isothermal conditions, while Figure 1b shows the simulated first-order data for nonisothermal conditions. Table 1 shows the values of E_a and ln A obtained after fitting the simulated first-order isothermal data to various models. Each model fits the data almost perfectly, which leads to two conclusions. First, each model gives the correct activation energy, 167.2 kJ/mol. Second, the frequency factors, A, do not differ significantly among the models. The exception is model F2, for which differences of 2

TABLE 8: Temperature Dependence of Some Functions of Fractional Conversion, x, in the Kinetic Data (from $x = 0.01$ to $x = 0.99$) for Three Simulated Processes, First-Order (F1), Fourth-Order Avrami−Erofeyev (A4), and One-Dimensional Diffusion (D1), under Nonisothermal Conditions (12 °C/min)

	F1		A4		D1	
Q(x)	R(dlnQ(x)/d(1/T)) (kJ/mol)	R^2	R(dlnQ(x)/d(1/T)) (kJ/mol)	R^2	R(dlnQ(x)/d(1/T)) (kJ/mol)	R^2
x	−139.60	0.978	−560.84	0.979	−86.98	1.000
$1 - x$	89.58	0.672	350.67	0.665	28.63	0.499
$-\ln(1 - x)$	−174.57	1.000	−698.81	1.000	−99.29	0.988
$(1 - x)^{-1/3} - 1$	−190.67	0.996	−761.84	0.996	−104.29	0.977
$(1 - x)\ln(1 - x) + x$	−297.19	0.988	−1194.22	0.988	−181.01	0.999
$1 - (1 - x)^{1/3}$	−160.81	0.997	−644.85	0.997	−94.75	0.995
$1 - (1 - x)^{1/2}$	−154.78	0.993	−621.32	0.993	−92.65	0.997
$1 - 2x/3 - (1 - x)^{2/3}$	−305.10	0.991	−1225.22	0.992	−183.80	0.998

TABLE 9: List of Reaction Models Commonly Used To Represent Solid-State Reaction Kinetics[1,2]

model	differential kinetic function, f(x)	integral kinetic function, g(x)	corresponding mechanism
A2	$2(1 - x)[-\ln(1 - x)]^{1/2}$	$[-\ln(1 - x)]^{1/2}$	Avrami−Erofeyev, $n = 2$
A3	$3(1 - x)[-\ln(1 - x)]^{2/3}$	$[-\ln(1 - x)]^{1/3}$	Avrami−Erofeyev, $n = 3$
A4	$4(1 - x)[-\ln(1 - x)]^{3/4}$	$[-\ln(1 - x)]^{1/4}$	Avrami−Erofeyev, $n = 4$
D1	$1/2x$	x^2	one-dimensional diffusion
D2	$[-\ln(1 - x)]^{-1}$	$(1 - x)\ln(1 - x) + x$	two-dimensional diffusion
D3	$(3/2)(1 - x)^{1/3}[(1 - x)^{-1/3} - 1]^{-1}$	$[1 - (1 - x)^{1/3}]^2$	three-dimensional diffusion (Jander)
D4	$(3/2)[(1 - x)^{-1/3} - 1]^{-1}$	$1 - 2x/3 - (1 - x)^{2/3}$	three-dimensional diffusion (Ginstling−Brounshtein)
F1	$1 - x$	$-\ln(1 - x)$	first-order reaction
F2	$(1 - x)^2$	$1/(1 - x) - 1$	second-order reaction
P1	$x(1 - x)$	$\ln[x/(1 - x)] + kt_{1/2}$	Prout−Tompkins
PL2	$2x^{1/2}$	$x^{1/2}$	power law ($n = 1/2$)
PL3	$3x^{2/3}$	$x^{1/3}$	power law ($n = 1/3$)
PL4	$4x^{3/4}$	$x^{1/4}$	power law ($n = 1/4$)
R1	1	x	one-dimensional phase boundary
R2	$2(1 - x)^{1/2}$	$1 - (1 - x)^{1/2}$	two-dimensional phase boundary
R3	$3(1 - x)^{2/3}$	$1 - (1 - x)^{1/3}$	three-dimensional phase boundary

orders of magnitude are apparent. When the added noise is removed from the simulated data, the conclusions are unchanged.

Table 2 lists the values of E_a and ln A obtained from fitting the simulated first-order data at a heating rate of 12 °C/min to the various kinetic models in their differential forms (eq 1). Several models, including the first-order reaction and the Avrami−Erofeyev equations with different orders, give an excellent fit ($R^2 > 0.999$) and are statistically indistinguishable. Contrary to fitting of the simulated isothermal data, fitting of the simulated nonisothermal data to different models results in very different values of the activation energy and frequency factor. For example, for three-dimensional diffusion (model D3) E_a is relatively large (298 kJ/mol), while for the power law models, PL3 and PL4, the E_a values are so low as to be negative. The frequency factor, A, also depends strongly on models to which the simulated first-order data are fitted.

Table 3 lists the values of E_a and ln A obtained by fitting the same simulated first-order data as in Table 2, but using the integral kinetic function (eq 2). As expected, the values of E_a and ln A still depend on the model. However, with the exception of a few models, including Avrami−Erofeyev models A2, A3, A4, and the exact model, F1, fitting to g(x) and f(x) leads to different values of E_a and A for the same model, which agrees with previous mathematical analysis. It is noted that the coefficient of determination, R^2, is much closer to 1.0 when the simulated data are fitted to g(x) rather than to f(x). Therefore, the integral form is less able to discriminate between the reaction models than the differential form. In other words, g(x) leads to greater ambiguity than f(x) in the selection of a reaction model. Therefore, it is recommended that f(x) be used in model-fitting when the number of data points is sufficient to allow for differentiation without causing too much noise. The differences among the values of E_a and A after fitting to differential and integral forms appear to eliminate some models. However, because of the influence of the experimental error on the values of E_a and A, this recommendation may not eliminate all the false models.

Tables 4 and 5 show the results of fitting the simulated fourth-order Avrami−Erofeyev kinetic data under isothermal conditions (Figure 2a) and nonisothermal conditions (Figure 2b), while Tables 6 and 7 show the results of fitting the simulated one-dimensional diffusion data under isothermal conditions (Figure 3a) and nonisothermal conditions (Figure 3b). The conclusions are essentially the same as those above, namely, isothermal data give model-independent E_a, whereas nonisothermal data give model-dependent E_a.

In the previous mathematical analysis, we showed that the fitted activation energy is equal to the true activation energy, E_a^0, plus the correction term, ΔE_a. We also argued that ΔE_a is zero for isothermal kinetic data but not zero for nonisothermal kinetic data. To demonstrate this concept, the simulated nonisothermal data conforming exactly to a first-order process by heating at 12 °C/min was applied to show the nonzero values of the correction terms for various models with respect to the exact model, the first-order reaction. Careful examination of the correction terms in Table 10 shows that all ln[f′(x)] and ln[g′(x)] functions are composed of relatively few elementary terms, such as ln x, ln(1 − x), ln[−ln(1 − x)]. It would be relatively simple to ascertain the temperature dependence of ln[f′(x)] or ln[g′(x)] if we knew the temperature dependence of each component, ln[Q(x)], such as ln x, ln(1 − x), ln[−ln(1 − x)], where Q(x) is a convenient symbol representing each simple term. Using the simulated nonisothermal first-order data at 12 °C/min, we obtained the temperature dependence of each Q(x) term by linear regression. Columns 2 and 3 of Table 8 list the results of the regression expressed as R dln[Q(x)]/d(1/T) and R^2, respectively. Most of the regressions give high

TABLE 10: Correction Term of the Models Listed in Table 9 with Respect to the First-Order Kinetic Model (F1)

model	$\ln[f'(x)]$[a]	$\ln[g'(x)]$[b]
A2	$\ln 2 + (1/2)\ln[-\ln(1-x)]$	$-(1/2)\ln[-\ln(1-x)]$
A3	$\ln 3 + (2/3)\ln[-\ln(1-x)]$	$-(2/3)\ln[-\ln(1-x)]$
A4	$\ln 4 + (3/4)\ln[-\ln(1-x)]$	$-(3/4)\ln[-\ln(1-x)]$
D1	$-\ln 2 - \ln x - \ln(1-x)$	$2\ln x - \ln[-\ln(1-x)]$
D2	$-\ln[-\ln(1-x)] - \ln(1-x)$	$\ln[(1-x)\ln(1-x) + x] - \ln[-\ln(1-x)]$
D3	$\ln(3/2) - (2/3)\ln(1-x) - \ln[(1-x)^{-1/3} - 1]$	$2\ln[1 - (1-x)^{1/3}] - \ln[-\ln(1-x)]$
D4	$\ln(3/2) - \ln[(1-x)^{-1/3} - 1] - \ln(1-x)$	$\ln[1 - 2x/3 - (1-x)^{2/3}] - \ln[-\ln(1-x)]$
F1[c]	0	0
F2	$\ln(1-x)$	$\ln x - \ln(1-x) - \ln[-\ln(1-x)]$
P1	$\ln x$	$\ln[\ln x - \ln(1-x)] - \ln[-\ln(1-x)]$
PL2	$\ln 2 + (1/2)\ln x - \ln(1-x)$	$(1/2)\ln x - \ln[-\ln(1-x)]$
PL3	$\ln 3 + (2/3)\ln x - \ln(1-x)$	$(1/3)\ln x - \ln[-\ln(1-x)]$
PL4	$\ln 4 + (3/4)\ln x - \ln(1-x)$	$(1/4)\ln x - \ln[-\ln(1-x)]$
R1	$-\ln(1-x)$	$\ln x - \ln[-\ln(1-x)]$
R2	$\ln 2 - (1/2)\ln(1-x)$	$\ln[1 - (1-x)^{1/2}] - \ln[-\ln(1-x)]$
R3	$\ln 3 - (1/3)\ln(1-x)$	$\ln[1 - (1-x)^{1/3}] - \ln[-\ln(1-x)]$

[a] $f'(x) = f(x)/f^0(x)$ is the correction term of the differential kinetic function with respect to the exact differential kinetic function $f^0(x)$. [b] $g'(x) = g(x)/g^0(x)$ is the correction term of the integral kinetic function with respect to the exact integral kinetic function $g^0(x)$. [c] Exact model is F1.

TABLE 11: Correction Term of the Models Listed in Table 9 with Respect to the Fourth-Order Avrami−Erofeyev Kinetic Model (A4)

model	$\ln[f'(x)]$[a]	$\ln[g'(x)]$[b]
A2	$-\ln 2 - (1/4)\ln[-\ln(1-x)]$	$(1/4)\ln[-\ln(1-x)]$
A3	$\ln(3/4) - (1/12)\ln[-\ln(1-x)]$	$(1/12)\ln[-\ln(1-x)]$
A4[c]	0	0
D1	$-\ln 8 - \ln x - \ln(1-x) - (3/4)\ln[-\ln(1-x)]$	$2\ln x - (1/4)\ln[-\ln(1-x)]$
D2	$-\ln 4 - \ln(1-x) - (7/4)\ln[-\ln(1-x)]$	$\ln[(1-x)\ln(1-x) + x] - (1/4)\ln[-\ln(1-x)]$
D3	$\ln(3/8) - (2/3)\ln(1-x) - \ln[(1-x)^{-1/3} - 1] - (3/4)\ln[-\ln(1-x)]$	$2\ln[1 - (1-x)^{1/3}] - (1/4)\ln[-\ln(1-x)]$
D4	$\ln(3/8) - \ln[(1-x)^{-1/3} - 1] - \ln(1-x) - (3/4)\ln[-\ln(1-x)]$	$\ln[1 - 2x/3 -(1-x)^{2/3}] - (1/4)\ln[-\ln(1-x)]$
F1	$-\ln 4 - (3/4)\ln[-\ln(1-x)]$	$(3/4)\ln[-\ln(1-x)]$
F2	$-\ln 4 + \ln(1-x) - (3/4)\ln[-\ln(1-x)]$	$\ln x - \ln(1-x) - (1/4)\ln[-\ln(1-x)]$
P1	$-\ln 4 + \ln x - (3/4)\ln[-\ln(1-x)]$	$\ln[\ln x - \ln(1-x)] - (1/4)\ln[-\ln(1-x)]$
PL2	$-\ln 2 + (1/2)\ln x - \ln(1-x) - (3/4)\ln[-\ln(1-x)]$	$(1/2)\ln x - (1/4)\ln[-\ln(1-x)]$
PL3	$\ln(3/4) + (2/3)\ln x - \ln(1-x) - (3/4)\ln[-\ln(1-x)]$	$(1/3)\ln x - (1/4)\ln[-\ln(1-x)]$
PL4	$(3/4)\ln x - \ln(1-x) - (3/4)\ln[-\ln(1-x)]$	$(1/4)\ln x - (1/4)\ln[-\ln(1-x)]$
R1	$-\ln 4 - \ln(1-x) - (3/4)\ln[-\ln(1-x)]$	$\ln x - (1/4)\ln[-\ln(1-x)]$
R2	$-\ln 2 - (1/2)\ln(1-x) - (3/4)\ln[-\ln(1-x)]$	$\ln[1-(1-x)^{1/2}] - (1/4)\ln[-\ln(1-x)]$
R3	$\ln(3/4) - (1/3)\ln(1-x) - (3/4)\ln[-\ln(1-x)]$	$\ln[1-(1-x)^{1/3}] - (1/4)\ln[-\ln(1-x)]$

[a] $f'(x) = f(x)/f^0(x)$ is the correction term of the differential kinetic function with respect to the exact differential kinetic function $f^0(x)$. [b] $g'(x) = g(x)/g^0(x)$ is the correction term of the integral kinetic function with respect to the exact integral kinetic function $g^0(x)$. [c] Exact model is A4.

TABLE 12: Correction Term of the Models Listed in Table 9 with Respect to the One-Dimensional Diffusion Model (D1)

model	$\ln[f'(x)]$[a]	$\ln[g'(x)]$[b]
A2	$\ln(1-x) - \ln x + (1/2)\ln[-\ln(1-x)]$	$(1/2)\ln[-\ln(1-x)] - 2\ln x$
A3	$\ln(3/2) + \ln(1-x) - \ln x + (2/3)\ln[-\ln(1-x)]$	$(1/3)\ln[-\ln(1-x)] - 2\ln x$
A4	$\ln 2 + \ln(1-x) - \ln x + (3/4)\ln[-\ln(1-x)]$	$(1/4)\ln[-\ln(1-x)] - 2\ln x$
D1[c]	0	0
D2	$-\ln 2 - \ln[-\ln(1-x)] - \ln x$	$\ln[(1-x)\ln(1-x) + x] - 2\ln x$
D3	$\ln(3/4) + (1/3)\ln(1-x) - \ln x - \ln[(1-x)^{-1/3} - 1]$	$2\ln[1 - (1-x)^{1/3}] - 2\ln x$
D4	$\ln(3/4) - \ln[(1-x)^{-1/3} - 1] - \ln x$	$\ln[1 - 2x/3 - (1-x)^{2/3}] - 2\ln x$
F1	$-\ln 2 + \ln(1-x) - \ln x$	$\ln[-\ln(1-x)] - 2\ln x$
F2	$-\ln 2 + 2\ln(1-x) - \ln x$	$-\ln(1-x) - \ln x$
P1	$-\ln 2 + 2\ln(1-x)$	$\ln[\ln x - \ln(1-x)] - 2\ln x$
PL2	$-(1/2)\ln x$	$-(3/2)\ln x$
PL3	$\ln(3/2) - (1/3)\ln x$	$-(5/3)\ln x$
PL4	$\ln 2 - (1/4)\ln x$	$-(7/4)\ln x$
R1	$-\ln 2 - \ln x$	$-\ln x$
R2	$(1/2)\ln(1-x) - \ln x$	$\ln[1 - (1-x)^{1/2}] - 2\ln x$
R3	$\ln(3/2) + (2/3)\ln(1-x) - \ln x$	$\ln[1 - (1-x)^{1/3}] - 2\ln x$

[a] $f'(x) = f(x)/f^0(x)$ is the correction term of the differential kinetic function with respect to the exact differential kinetic function $f^0(x)$. [b] $g'(x) = g(x)/g^0(x)$ is the correction term of the integral kinetic function with respect to the exact integral kinetic function $g^0(x)$. [c] Exact model is D1.

R^2, except when $Q(x) = (1 - x)$. However, the extent of the correlation is not important here, because we wish to obtain the contribution of each term to the activation energy in the overall model-fitting. By adding the contribution of each term in $\ln[f'(x)]$ or $\ln[g'(x)]$, we obtain the correction term of the activation energy, ΔE_a, for each model (Tables 2 and 3). When this ΔE_a is added to the true activation energy, $E_a^0 = 167.2$ kJ/mol, the fitted apparent E_a is then obtained and is placed in the last column of Table 2 or Table 3. The apparent E_a values in Tables 2 and 3 are in good agreement. This treatment demonstrates how the model-dependent apparent E_a arises in fitting of nonisothermal data. As before, the conclusions are unchanged when the added noise is removed from the simulated data.

An analogous study was carried out for the simulated fourth-order Avrami−Erofeyev kinetic data at 12 °C/min (Tables 4, 5, and 8) and the simulated one-dimensional diffusion process at 12 °C/min (Tables 6−8). These results can be interpreted in the same way as for the simulated first-order data shown above. Therefore, it appears that the above treatment and interpretation should be generally valid.

It should be mentioned that nonisothermal kinetic data are equally as informative as isothermal kinetic data, although the strong model-dependence of the kinetic parameters makes the kinetic analysis more difficult and challenging. Other approaches, such as Kissinger analysis[29,30] and model-free analysis,[9,14,31−34] can be successfully applied to extract the correct kinetic information from nonisothermal data.

Conclusions

The following conclusions can be drawn from mathematical analysis of model-fitting to solid-state kinetic data and are verified with the simulated data.

(1) The activation energy obtained from fitting of isothermal kinetic data is independent of the model to which the data are fitted. (2) The frequency factor obtained from fitting of isothermal kinetic data depends not strongly on the model to which the kinetic data are fitted. (3) The activation energy and frequency factor obtained by fitting nonisothermal kinetic data depend strongly on the model to which the data are fitted. (4) The conclusions are unchanged when noise at the level of ±0.1% of the maximum value, $\alpha = 1$, was added to every simulated data point.

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