4692 *Chem. Mater.* **2009,** *21,* 4692–4705
DOI:10.1021/cm9018716

CHEMISTRY OF MATERIALS
Article

# Is There a Minimal Chemical Mechanism Underlying Classical Avrami-Erofe'ev Treatments of Phase-Transformation Kinetic Data?

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*Received June 29, 2009*

We report herein our efforts to see if there is not a minimal chemical mechanism that can provide statistically equivalent fits to solid-state and other phase-transformation kinetic data classically treated by the Avrami-Erofe'ev (A-E) kinetic model or its derivatives. Doing so is an important, missing piece of attempts to fit and draw chemical insight from solid-state kinetics, as made apparent by citations and quotations from the literature which detail the presently confused state of solid-state kinetics and, especially, what those kinetics mean in terms of the underlying chemical mechanism(s). Specifically, we test herein the one available, *minimalistic, chemical-mechanism-based* kinetic model that is able to deconvolute nucleation from growth, a model originally developed for transition-metal nanocluster nucleation and growth in solution, $A \rightarrow B$ (rate constant $k_1$) then $A + B \rightarrow 2B$ (rate constant $k_2$). The two-step model tested is able to fit solid-state phase transformation kinetic data equally well in comparison to fits obtained using the classic A-E equation from the 1940s. Statistically, it is found that the A-E equation is statistically significantly superior for 4 of 12 literature data sets examined, but that the two-step chemical mechanism-based model (known as the Finke-Watzky (F-W) model) is statistically significantly better for 2 of those 12 data sets, and the models give arguably indistinguishable fits within experimental error to the other 6 data sets. The results provide credence to the hypothesis that the two models can be viewed as different descriptions of the same underlying chemical and physical processes. Given the evidence that the chemical-mechanism-based two-step model provides equivalent (to sometimes better) fits within experimental error in 8 of the 12 cases examined, but that the A-E and integrated F-W equations were then mathematically equated to see if this provides any insights into the question of the physical meaning of the A-E parameters $k$ and $n$. The math reveals that the A-E parameters $k$ and $n$ can be viewed as containing a complex convolution of the F-W chemical rate constants $k_1$ and $k_2'$ (where $k_2' = k_2[A]_0$ of the F-W model)—at least under the experimentally supported assumption that the A-E and F-W equations are somehow equivalent. Simulated A-E data for selected values of A-E parameters $k$ and $n$ (that give representative sigmoidal kinetic curves), followed by fits of those simulated curves to the F-W model and then plotting the resultant F-W $k_1$ and $k_2'$ rate constants as a function of the A-E $k$ and $n$ variables, provides additional interesting evidence that the A-E $k$ and $n$ and F-W $k_1$ and $k_2'$ can be viewed as complex convolutions of one another. Specifically, $k$ from this treatment appears as a convolution of $k_1$, $k_2'$, and $n$ (as well as time, $t$) and $n$ as a convolution of $k_1$, $k_2'$, and $k$ (as well as $t$). A discussion of the advantages and limitations of each model is presented followed by a summary of the conclusions from the present studies. The significance of the results is twofold: (i) there is now an experimentally supported way to deconvolute an average nucleation, $k_1$, from an average autocatalytic growth, $k_2$, rate constant from solid-state kinetic data, and importantly, (ii) there now are experimentally supported and rigorously defined words/concepts that can be used to support the discussion of those rate constants in terms of the underlying physical processes, namely, "nucleation" and "autocatalytic growth". These are not trivial results in light of concepts such as "autocatalytic nucleation" that continue to be used without adequate experimental support and which, therefore, continue to cause confusion in the solid-state kinetics literature. A section listing important caveats to this work apparent from examining the solid-state kinetic literature, plus a look ahead to needed future work, is also briefly presented.

## Introduction

We report herein our search to see if there is not a minimal chemical mechanism that can give equivalent fits to, and therefore by all appearances could be viewed as underlying, solid-state kinetic data traditionally fit by the Avrami-Erofe'ev (A-E) equation (see Table S1 of the Supporting Information for a historical tabulation of the A-E equation, eq 1,[1] and its more than 13 variants).[2-4]

$$\ln(1-\alpha) = -(kt)^n \tag{1}$$

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The chemical-mechanism-based, minimalistic kinetic model that we have examined is the Finke-Watzky (hereafter F-W) two-step kinetic scheme consisting of nucleation followed by autocatalytic growth, Scheme 1.[5−8] We also look at the mathematical relationship between the A-E and F-W treatments to see if the A-E parameters $k$ and $n$ can be expressed and thus at least conceivably understood somewhat better (or at least differently) in terms of the F-W rate constants for nucleation ($k_1$) and autocatalytic growth ($k_2$), Scheme 1 (or actually $k_2' = k_2[\mathrm{A}]_0$, vide infra). This is of some significance since A-E treatments often talk of "nucleation and growth", but *contain only a single rate parameter, k,* a practice that causes considerable confusion,[2−4] a confusion that originally drew us to this problem: *how is it possible to talk about two chemical processes with only one rate constant? Something must be amiss here!?* Simulations of kinetic data generated by the A-E equation for selected $k$ and $n$ values that give sigmoidal curves, followed by fitting those simulated curves with the F-W model, are also employed to gain possible insight into the relationship between the A-E parameters $k$ and $n$ in terms of the F-W $k_1$ and $k_2'$ rate constants. We also briefly discuss the plus/minus features of both the A-E and F-W treatments and look ahead to possible new, future directions that the present findings might allow. Caveats in the present work that are apparent from examination of the complicated, sometimes confusing, and often controversial area solid-state kinetics[9,10] are also provided and briefly discussed.

**Scheme 1. Finke-Watzky Two-Step Kinetic Model of Nucleation ($k_1$) and Autocatalytic Growth ($k_2$)[5]**

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$

$$\mathrm{A+B} \xrightarrow{k_2} \mathrm{2B}$$

The potential significance of attempts such as the present work to bring more chemical mechanisms to solid-state kinetics is presaged by Galweys' insightful comments[9] illustrating the confusion that exists at present in the area of at least nonisothermal solid-state reaction kinetics. Notable are his points: that chemical reaction mechanisms are too often missing, that "the consideration of alternative possibilities (i.e., mechanisms) is frequently ignored...", or even that the term "mechanism" has

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(1) (a) Herein we use Khanna and Taylor's[1b] modified form of the Avrami equation which, after slight rearrangment of eq 1 in the main text, is $\alpha = 1 - \exp\{-(kt)^n\}$. This form allows $k$ to be in units of time$^{-1}$ and is recommeded by Khanna and Taylor[1b] as well as by Galwey,[1c] although it is not preferred by others[1d] (albeit only for reasons that are a matter of preference in the final analysis[1d]). The original Avrami equation is $\alpha = 1 - \exp\{-k't^n\}$. These two equations are equivalent if $k' = k^n$, although the use of these two equations does cause confusion in the solid-state kinetics literature since the resultant $k$ and $k'$ have different values and units. Of interest and relevance to the present study is that Khanna and Taylor's modified Avrami equation was proposed in at attempt to make the resultant parameters one obtains closer *to being physically relevant/reasonable* for industrial polymer crystallization data.[1b] (b) Khanna, Y. P.; Taylor, T. J. *Polym. Eng. Sci.* **1988**, *28*, 1042–1045. (c) Galway, A. K. *Thermochem. Acta* **2004**, *413*, 160–183 (see pp 160−161, sections 5.5.1 and 5.5.2) . (d) Marangoni, A. G. *J. Am. Oil Chem. Soc.* **1998**, *75*, 1465–1467 (Marangoni admits in his paper that "From a curve-fitting point of view, there are no differences between these two functions") .

(2) (a) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103. (b) Avrami, M. *J. Chem. Phys.* **1940**, *8*, 212. (c) Avrami, M. *J. Chem. Phys.* **1941**, *9*, 177.

(3) Fanfoni, M.; Tomellini, M. *Il Nuovo Cimento* **1998**, *20*, 1171.

(4) (a) Jun, S.; Zhang, H.; Bechhoefer, J. *Phys. Rev. E.* **2005**, *71*, 011908. (b) Brown, M. E. *Thermochim. Acta* **1997**, *300*, 93. (c) Galwey, A. K.; Brown, M. E. Thermal Decomposition of Ionic Solids. *Studies in Physical and Theoretical Chemistry, 86*; Elsevier: New York, 1999; Chapter 3, pp 75−115.(d) Galwey, A. K. J. *Therm. Anal. Calorim.* **2008**, *92*, 967–983. (e) Khawam, A.; Flanagan, D. R. *J. Phys. Chem. B* **2006**, *110*, 17315–17328.

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(6) Finke, R. G. In *Metal Nanoparticles: Synthesis, Characterization, and Applications*; Feldheim, D. L., Foss, C. A., Jr., Eds.; Marcel Dekker: New York, 2001; Chapter 2.

(7) (a) Besson, C.; Finney, E. E.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 8179. (b) Besson, C.; Finney, E. E.; Finke, R. G. *Chem. Mater.* **2005**, *17*, 4925.

(8) (a) It has recently come to our attention[8f] that early work by Perez-Benito et al.[8a−e] on $\mathrm{MnO_4^-}$ oxidations of, for example, $\mathrm{Me_2NH}$, provides what can now be recognized as an early example of the two-step "F-W mechanism" utilized herein. The Perez-Benito work seems to have been generally missed in the particle nucleation and growth literature for perhaps four reasons: (i) the early work fails to reference or tie into any prior particle formation literature of the time (e.g., LaMer's work); (ii) nucleation and growth are not mentioned in the early work, (iii) that work[8b,c] never recognized nor wrote a generalized form of mechanism, that is the A → B, A + B → 2B that was conceptualized in our 1997 paper[5] (instead it gives only a differential equation, "$r=k_1c + k_2(c(c_0 - c)$", [8d] that one has to, and now can upon re-examination of that work, recognize as corresponding to the two-step mechanism denoted the "F-W mechanism" herein); and perhaps most importantly (iv) that work does not investigate, nor therefore recognize, the broad applicability of the two-step mechanism.[5,12−14] We even referenced one of Perez-Benito's papers[8b] in our early 1994 paper[35b] that had a non-generalized version of the two-step mechanism in it, but cited that paper as reference therein in regards to light scattering by the observed product, but not in any reference to their kinetics of mechanism which did not seem directly applicable at the time—in hindsight an error for which we apologize to Prof. Perez-Benito and his co-authors; the oversight was not intentional. We plan a badly needed review of the history leading up to the two-step mechanism, in which we will be sure that Perez-Benito and co-workers receive proper credit for their early work.(b) Mata-Perez, F.; Perez-Benito, J. *Z. Phys.Chem.* **1984**, *141*, 213–219. (c) Mata-Perez, F.; Perez-Benito, J. F. *J. Chem. Educ.* **1987**, *64*, 925–927. (d) Perez-Benito, J.; Arias, C. *Int. J. Chem. Kinet.* **1991**, *23*, 717–732. (e) There are several other papers in this series by Perez-Benito and co-authors; the latest is Insausti, M. J.; Mata-Perez, F.; Alvarez-Macho, M. P. *Collect. Czech. Chem. Commun.* **1996**, *61*, 232–241.(f) We thank Dr. Pete Skrdla for pointing out the J. Chem. Educ. reference[8c] to us and in turn thank Prof. Brown[10] who we understand first brought that reference to Dr. Skrdla's attention. There is truly an enormous, diffuse/largely unconnected, often conflicting or confusing literature of nucleation and growth phenomenon across nature, a literature we are doing our best to comprehend, connect, and distill[5−7,12−14,33−35,41] to its underlying essences, including the present contribution.

(9) Galwey, A. K. *Thermochim. Acta* **2004**, *413*, 139.

(10) (a) Brown notes, as the introduction to his paper,[10b] that "When one attempts to read the intimidating and rather indigestible literature of kinetics of solid-state processes and, in particular the papers on non-isothermal kinetics (NIK), one can not help noticing the similarities between Science and Religion. Those that believe that they have found the 'true way' promote their points-of-view with evangelistic fervor and often mention with contempt, or even attack, the practices of the 'heathen'. The field is full of dogma: 'Thou shall do this ... and thou shall not do the other'! An agnostic in the field (defined as a person who is uncertain or noncommittal) searches, perhaps in vain, for what is useful and what is not". We agree; the above quote pretty much explains why we are only now publishing the present contribution despite starting it in 2003 when we first realized that A-E and F-W provided equivalent fits in at least a number of instances to both solution nanocluster and solid-state sigmoidal kinetic data. Hence, our approach to the present paper can be described using the above language as that of (hopefully) "non-evangelical agnostics". (b) Brown, M. E. *J. Therm. Anal.* **1997**, *49*, 17–32.

lost its original and rigorous meaning in the area of solid-state thermal analysis kinetics.[9] Galwey has also noted in a 2008 review (see p 981[4d]) that it is important for kinetic investigations of solid-state reactions to be able to "distinguish... the roles of nucleation and of growth"—again we see the problem of the A-E treatment providing only a single rate parameter, $k$. In another classic treatment, Galwey and Brown note that there is a "need for greater emphasis on chemical, rather than *mathematical*, representations"[4c] (i.e., of solid-state reaction kinetics). Brown's introduction in his 1997 paper "Steps in a Minefield. Some Kinetic Aspects of Thermal Analysis", reproduced in a footnote for the interested reader, is also noteworthy—indeed, Brown's paper and its many insights and telling quotes are a must read for anyone interested in solid-state kinetics.[10]

The results presented herein provide, as their bottom lines and significance, (i) the ability to deconvolute a nucleation from an (autocatalytic) growth rate constant for solid-state kinetic data, and even more significantly (ii) experimental evidence for the use of the words/concepts of nucleation *and* autocatalytic growth in describing the results—both nontrivial accomplishments in the history of solid-state kinetics, so far as we can tell. The results presented herein are also of broader interest beyond solid-state kinetics since sigmoidal-type growth curves are ubiquitous throughout nature,[5−7,11−14] yet it has not proven possible until now to generally deconvolute even an average, *chemical-mechanism-based* nucleation rate constant from an average (autocatalytic, vide infra) growth rate constant. Cases where the "Ockham's razor"-based two-step F-W kinetic model employed herein has been able to quantitatively fit sigmoidal growth curves, while also deconvoluting (average) nucleation from (average) autocatalytic growth, include (originally) transition-metal nanocluster formation,[5−7,11] more recently protein aggregation involved in a wide variety of neurological diseases including Alzheimer's, Parkinson's, Huntington's, and prion-based diseases,[11−13] and now solid-state kinetic data.

## Experimental Section

**Selection of the Data To Be Fit.** We selected several solid-state kinetic studies from the literature, in which the A-E equation or some variation of it was used to fit the data. We digitized the data from the literature using DigitizeIt version 1.5.8. We fit the data from those systems using the A-E equation and the F-W model and compared the two to see which, if either, gave a superior fit. Seven of these systems are given in the main text herein, and five additional systems are provided in the Supporting Information. We also fit kinetic data for the formation of $\mathrm{Ir}^0_{\sim 300}$ nanoclusters[5] using both the F-W model and the A-E equation to show that both models can fit that data as well, vide infra.

**Data Anlysis.** The data from the solid-state reactions are typically given in terms of the amount of starting material transformed into product, $\alpha$, which *increases* with time. In the Avrami equation, then, $\alpha$ also increases with time. The F-W model, in comparison, historically has fit data for the *loss* of concentration of nanocluster precursor, A in Scheme 1. The integrated rate equation for the loss of A over time is given in eq 2.[5]

$$[\mathrm{A}]_t = \frac{\frac{k_1}{k_2} + [\mathrm{A}]_0}{1 + \frac{k_1}{k_2[\mathrm{A}]_0}\exp[(k_1 + k_2[\mathrm{A}]_0)t]} \tag{2}$$

To compare fits between the F-W model and the A-E equation, eq 2 can be converted to a form that expresses $\alpha$ as a function of time, by recognizing that in the F-W model, $\alpha = ([\mathrm{A}]_0 - [\mathrm{A}]_t)/[\mathrm{A}]_0$. To get eq 3, then, we simply set $[\mathrm{A}]_t = [\mathrm{A}]_0(1 - \alpha)$ on the left-hand side of eq 2 and then solved the equation for $\alpha$. Note that in eq 3 we have necessarily defined $k_2' = k_2[\mathrm{A}]_0$; this removes the concentration dependences from the F-W model as is necessary since concentration is not a useful concept in the solid-state. The resulting eq 3 in turn allows the F-W and A-E models to be directly compared.

$$\alpha = 1 - \frac{k_1 + k_2'}{k_2' + k_1\exp[(k_1 + k_2')t]} \tag{3}$$

Note that in eq 3 the units of $k_1$ are time$^{-1}$ while the units of $k_2' = k_2[\mathrm{A}]_0$ are now also time$^{-1}$ (vs the units in eq 2 of the rate constants for nucleation and growth of nanoclusters $k_1$ and $k_2$ of time$^{-1}$ and M$^{-1}$ time$^{-1}$, respectively). In the A-E equation, the parameter $n$ is unitless, while the units of $k$ are time$^{-1}$.

Nonlinear least-squares curve fitting of the data was accomplished using Microcal Origin version 7.0. The data examined herein are fit using eq 1 for the A-E equation and eq 3 for the F-W two-step kinetic model.

Statistical judgment of the quality of the fits was performed for each system in two ways. First, values of $R^2$, the coefficient of determination, were calculated using eq 4.

$$R^2 = 1 - \frac{\mathrm{SS}}{\mathrm{SS}_{\mathrm{tot}}} \tag{4}$$

The residual sum-of-squares, SS, is given by $\mathrm{SS} = \sum_{i=1}^{N}(y_i - f_i)^2$, where $y$ is the experimental value and $f$ is the value predicted from the model. The total sum-of squares, $\mathrm{SS}_{\mathrm{tot}}$, is given by $\mathrm{SS} = \sum_{i=1}^{N}(y_i - \bar{y})^2$, where $\bar{y}$ is the average of all of the data values. Values of $R^2$ closer to 1 indicate a closer correlation and therefore a better fit for the model employed. The other statistical method employed was Akaike's Information Criterion (AIC).[15]

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(11) For a list of lead references to sigmoidal curves in nature, see elsewhere[12−14,43] as well as refs 1−11 summarized in Finney, E. E.; Finke, R. G. Fitting and Interpreting Transition-Metal Nanocluster Formation and Other Sigmoidal-Like Kinetic Data: A More Thorough Testing of Dispersive Kinetics vs Chemical-Mechanism-Based Equations and Treatments. *Chem. Mater.* **2009**, DOI: 10.1021/cm901142p.

(12) Morris, A. M.; Watzky, M. A.; Agar, J. N.; Finke, R. G. Biochemistry **2008**, *47*, 2413 and references therein.

(13) Watzky, M. A.; Morris, A. M.; Ross, E. D.; Finke, R. G. *Biochemistry* **2008**, *47*, 10790–10800.

(14) Morris, A. M.; Watzky, M. A.; Finke, R. G. *Biophys. Biochem. Acta* **2009**, *1794*, 375–397.

(15) (a) Burnham, K. P.; Anderson, D. R. *Model Selection and Multimodel Inference: A Practical Information-Theoretic Approach*, 2nd Ed.; Springer-Verlag: New York, 2002.(b) Motulsky, H.; Christopoulos, A. *Fitting Models to Biological Data Using Linear and Nonlinear Regression*; Oxford: New York, 2004.(c) Bozdogan, H. *J. Math. Psych.* **2000**, *44*, 62.(d) A useful, readable introduction to both model building and testing, including the AIC method, is Motulksy, H. J.; Christopoulos, A. *Fitting models to biological data using linear and nonlinear regression. A practical guide to curve fitting*; GraphPad Software Inc.: San Diego, CA, 2003 (www.graphpad.com); see pp 134−165.

This method calculates the probability that one model should be used over another for a given data set. More specifically, we used Akaike's second-order method, eq 5, to calculate values of AICc for each model.

$$\mathrm{AICc} = N \ln\left(\frac{\mathrm{SS}}{N}\right) + 2\mathrm{K} + \frac{2K(K+1)}{N - \mathrm{K} - 1} \qquad (5)$$

In eq 5, N is the number of data points, SS is the residual sum-of-squares as defined above, and $K$ is the number of parameters in each model. Because lower SS values correspond to better fits and because eq 5 imposes a positive penalty for a model with more parameters, the model with the lowest value of AICc will be statistically favored. To make this determination more quantitative, one can convert the differences in AICc values to Akaike weights, $w$ (between 0 and 1), eq 6, which represents the likelihood (i.e., the relative probability) that a given model is favored.[15]

$$w = \frac{\exp(-\Delta \mathrm{AICc}_i/2)}{\sum_{r=1}^{R} \exp(-\Delta \mathrm{AICc}_r/2)} \qquad (6)$$

Here, $\Delta\mathrm{AICc}_i = \mathrm{AICc}_i - \mathrm{AICc}_{\mathrm{min}}$, where $\mathrm{AICc}_{\mathrm{min}}$ is the lowest AICc value. In effect, the Akaike weight is a relative probability that a given model is the best one of those considered by this established statistical approach for model comparisons. One can then construct "evidence ratios", ER, from the relative ratios of the $w$ values, and in what follows we will give $\mathrm{ER}_{(\mathrm{A\text{-}E/F\text{-}W})}$, the ratio of the A-E $w$ value to the F-W $w$ value.

Note that the use of the exponential in calculating $w$ significantly magnifies any difference in AICc values, making the $w$ value enormously more sensitive to differences in fit quality than the (relatively insensitive) $R^2$ value. For example, we will see examples in what follows where small differences of *only* $\Delta R^2 = -0.0012$ correspond to a $\mathrm{ER}_{(\mathrm{A\text{-}E/F\text{-}W})} \sim 10^{-16}$ in favor of the F-W model, while an *even smaller* $\Delta R^2 = +0.0005$ in another case corresponds to a $\mathrm{ER}_{(\mathrm{A\text{-}E/F\text{-}W})} \sim 10^{15}$ in favor of the A-E model. In addition, five of the $\mathrm{ER}_{(\mathrm{A\text{-}E/F\text{-}W})}$ values in what follows are between 0.37 to 52, one is 588, and one is 4554. Since we do not believe that $w$ values smaller than $w = 10^{\pm 4}$ are different beyond the experimental error of the data and fits, we have called the seven values of $w$ that are not at least $w \geq 10^{\pm 4}$ as "equivalent within experimental error". Supporting this (admittedly somewhat arbitrary at present) treatment is our initial experience with AICc ER values elsewhere (a relatively rare use of AICc for such chemical systems) in which the ER values are $10^{-38}$ to $10^{-184}$.[11] That said, much more experience with chemical systems and the AICc treatment will be needed before it is known if the above cutoff of "experimentally significantly different $\mathrm{ER}_{(\mathrm{A\text{-}E/F\text{-}W})}$ values have $\mathrm{ER} \geq 10^{\pm 4}$" is a good versus a poor assumption.

**A-E Curve Simulations Followed by Fitting with the F-W Model in Search of the Connections between the A-E Parameters $k$ and $n$ and the F-W $k_1$ and $k_2'$.** Kinetic data were simulated using the A-E equation, eq 1, in Microsoft Excel. A series of α versus time data were generated, starting with $k = 0.1$ and $n = 3$. The α versus time data were then imported into Origin and fit using the F-W model, eq 3, to obtain the corresponding values of $k_1$ and $k_2'$. Then, the parameters $k$ and $n$ were varied independently while keeping the other parameter constant to generate new α versus time data, with subsequent fits to the F-W model. Using the data obtained by this method, plots of $k_1$ and $k_2'$ versus $k$ at constant $n$ and plots of $k_1$ and $k_2'$ versus $n$ at constant $k$ were made. These plots are shown in Figure 9.

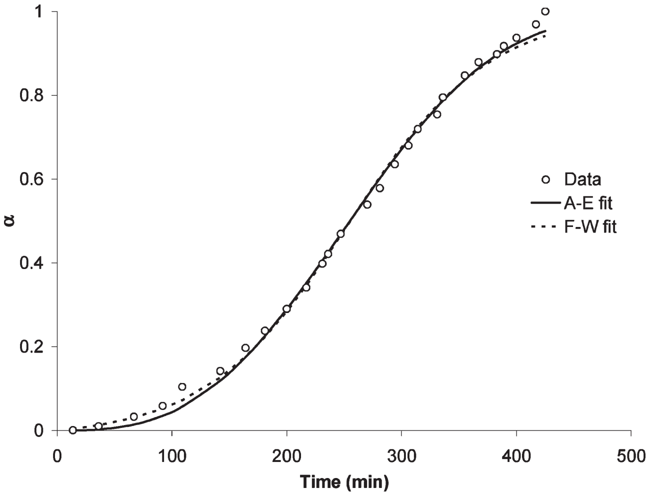

**Figure 1.** Kinetic data for the cubic and tetragonal phases of $Bi_3NbO_7$, with fits to the A-E equation (with $n = 2.91(7)$ and $k = 0.00346(2)$ min$^{-1}$) and to the F-W model (with $k_1 = 2.6(2) \times 10^{-4}$ min$^{-1}$ and $k_2' = 0.0160(5)$ min$^{-1}$). The statistics of the fits are given in Table 1.

## Results and Discussion

The seven literature systems examined below, along with the five additional systems examined in the Supporting Information, were examined by fitting the data to the A-E equation and also to the F-W model and then looking at the resulting statistics of the fits as well as simply examining the fits visually to develop an intuition for the quality of the fits and the resultant statistics.

**Phase Transformation of $Bi_3NbO_7$.** Lacorre et al. studied the transition between the metastable cubic and the stable tetragonal phases of $Bi_3NbO_7$; the significance of the tetragonal phase is that it has a higher electronic conductivity than the cubic phase.[16] The transition was carried out at four different temperatures, and the kinetics were analyzed by Lacorre et al. using the A-E equation. As is common in the solid-state literature, those authors linearized the fit in the following way: taking the ln of both sides of eq 1 gives eq 7 so that a plot of $\ln[-\ln(1-a)]$ versus $\ln(t)$ is a straight line with slope $n$ and intercept $n\ln(-k)$ via a linearized ln−ln plot. The plot was approximately linear for $0.05 \leq \alpha \leq 0.90$. For the transformation at 840 °C, the A-E parameters obtained were $n = 2.60$ and $k = 5.66 \times 10^{-5}$ min$^{-1}$.

$$\ln[-\ln(1-\alpha)] = n\ln(k) + n\ln(t) \qquad (7)$$

When we fit the entire sigmoidal data set, without linearization of it, we obtained the curve and the A-E parameters given in Figure 1c, $n = 2.91(7)$ and $k = 0.00346(2)$ min$^{-1}$. Note the value that we obtained for $n$ is close to that obtained from the linearized data, but the values of $k$ are different by more than $10^2$. This shows the significance of fitting the *entire* data set and not just the data that can be linearized. (Of course, and since nonlinear least-squares is now readily available, one never wants to take a highly nonlinear, sigmoidal curve and

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(16) Wang, X. P.; Corbel, G.; Kodjikian, S.; Fang, Q. F.; Lacorre, P. *J. Solid State Chem.* **2006**, *179*, 3338.

**Table 1. Statistical Data for the Fits in the Systems Described Herein to the A-E Equation and the F-W Model**

| system (figure) | $R^2$ (A-E) | $R^2$ (F-W) | AICc (A-E) | AICc (F-W) | *w* (A-E) | *w* (F-W) | $\mathrm{ER}_{(\text{A-E/F-W})}$ |
|---|---|---|---|---|---|---|---|
| $Bi_3$ *1* | 0.9967 | 0.9965 | −210 | −208 | 0.71 | 0.29 | 2.5 |
| Zr *2* | 0.9982 | 0.9994 | −544 | −617 | $1.1 \times 10^{-16}$ | 1 | $1.1 \times 10^{-16}$ |
| $CuAlCl_4$ *3* | 0.9969 | 0.9944 | −223 | −206 | 0.9997 | 0.0003 | 4554 |
| polymer *4* | 0.9999 | 0.9995 | −570 | −508 | 1 | $4.1 \times 10^{-14}$ | $2.4 \times 10^{13}$ |
| $Al_{75}$ *5* | 0.9968 | 0.9953 | −152 | −145 | 0.97 | 0.03 | 41 |
| $Fe_{80}$ *6* | 0.9999 | 0.9994 | −452 | −380 | 1 | $3.4 \times 10^{-16}$ | $2.9 \times 10^{15}$ |
| $Pd_{79}$ *7* | 0.9992 | 0.9985 | −423 | −385 | 1 | $5.6 \times 10^{-9}$ | $1.8 \times 10^{8}$ |

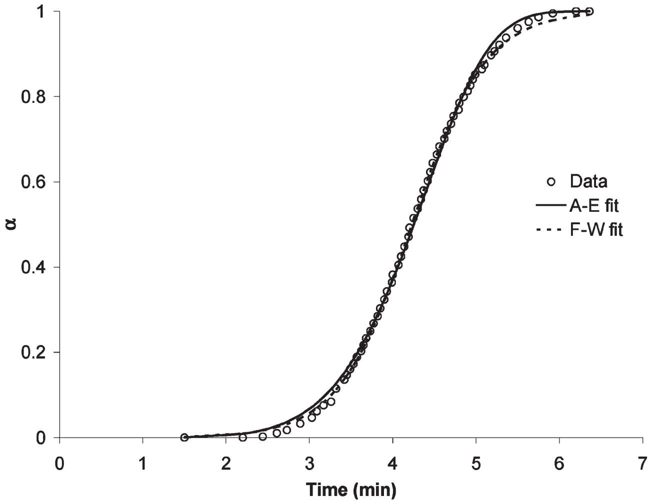

**Figure 2.** Kinetic data for the solid crystallization of bulk amorphous $Zr_{55}Cu_{30}Al_{10}Ni_5$, with fits to the A-E equation (with $n = 6.57(7)$ and $k = 0.2223(3)\ \mathrm{min}^{-1}$) and to the F-W model (with $k_1 = 1.54(9) \times 10^{-4}\ \mathrm{min}^{-1}$ and $k_2' = 2.27(1)\ \mathrm{min}^{-1}$). The statistics of the fits are given in Table 1.

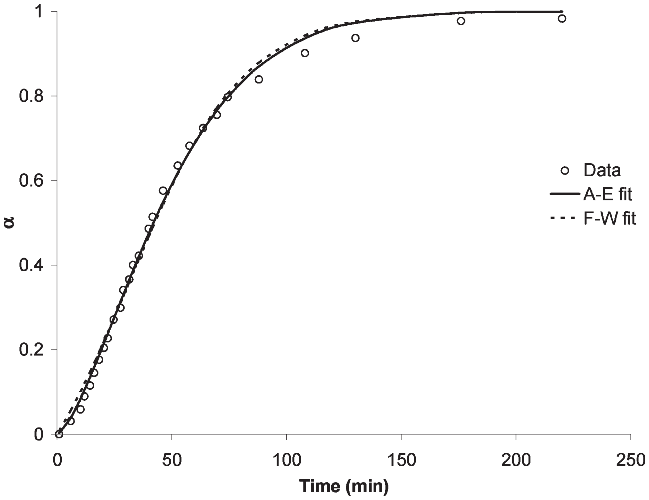

**Figure 3.** Kinetic data for the solid-state phase transition from $\beta$ to α phases of $CuAlCl_4$, with fits to the A-E equation (with $n = 1.46(3)$ and $k = 0.0185(2)\ \mathrm{min}^{-1}$) and to the F-W model (with $k_1 = 0.0089(5)\ \mathrm{min}^{-1}$ and $k_2' = 0.031(2)\ \mathrm{min}^{-1}$). The statistics of the fits are given in Table 1.

analyze it by a linearized function.) Fitting the same data using the F-W model gives the fit and rate constants also shown in Figure 1, $k_1 = 2.6(2) \times 10^{-4}\ \mathrm{min}^{-1}$ and $k_2' = 0.0160(5)\ \mathrm{min}^{-1}$. The statistics of the fits, given in Table 1, shows that the A-E equation and the F-W model give essentially equal fits within experimental error (i.e., the A-E equation is "preferred" only by an almost surely truly insignificant factor of 2.5). That is, the A-E and F-W models are equivalent for the purposes of fitting the data in Figure 1.

**Crystallization of $Zr_{55}Cu_{30}Al_{10}Ni_5$.** Liu et al. reported a study of the kinetics of the crystallization of bulk amorphous $Zr_{55}Cu_{30}Al_{10}Ni_5$, which follows sigmoidal-like kinetics.[17] For seven different temperatures between 466 and 480 °C, kinetic data were linearized and fit to the A-E equation. We chose the data taken at 470 °C for comparison between the linearized A-E fit, the full sigmoidal data A-E fit, and the F-W fit. For the linearized data, $n = 3.05$ and $k = 0.42\ \mathrm{min}^{-1}$.

When we fit the sigmoidal data to the A-E equation, we obtained the parameters $n = 6.57(7)$ and $k = 0.2223(3)\ \mathrm{min}^{-1}$, Figure 2, which are quite different from the parameters obtained from the linearized fit. We also fit the data to the F-W model, Figure 2, and obtained the rate constants $k_1 = 1.54(9) \times 10^{-4}\ \mathrm{min}^{-1}$and $k_2' = 2.27(1)\ \mathrm{min}^{-1}$. For this system, the F-W model is statistically preferred over the A-E equation by what is interpreted as a significant factor of $\sim 1 \times 10^{16}$, Table 1, even though the $\Delta R^2$ $(= R^2_{(\text{E-R})} - R^2_{(\text{F-W})})$ value in Table 1 is only $\Delta R^2 = -0.0012$.

**Phase Transition of $CuAlCl_4$.** In a careful study, Martin et al. studied the transition between the $\beta$ and α phases of $CuAlCl_4$ upon exposure to ethylene using X-ray diffraction and $^{63}$Cu NMR.[18] The transition showed sigmoidal-like kinetics at various temperatures, and Martin and co-workers fit the data in the usual way using the A-E equation. The data were linearized with a ln−ln plot between $0.15 \leq \alpha \leq 0.5$ and fit using linear regression. Only an average value was given for $n$ (1.5), so we performed a linear regression analysis for one of the data sets (the transition at 125 °C measured using $^{63}$Cu NMR) and obtained $n = 1.7$ and $k = 3.3 \times 10^{-4}\ \mathrm{min}^{-1}$ for this linearized data set. It should be noted that using the linearized form of the data removes the period from $\alpha = 0$ to $\alpha = 0.15$, effectively removing nucleation from the data.

Fitting all of the data to the A-E equation gives the curve shown in Figure 3, with $n = 1.46(3)$ and $k = 0.0185(2)\ \mathrm{min}^{-1}$. Fitting the data with the F-W model gives the curve also shown in Figure 3, with $k_1 = 0.0089(5)\ \mathrm{min}^{-1}$ and $k_2' = 0.031(2)\ \mathrm{min}^{-1}$. The statistics of the fits, given in Table 1, show that the A-E equation has at best a slight statistical edge over the F-W model of ~4554, although both models provide good visual fits to the data.

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(17) Liu, L.; Wu, Z. F.; Zhang, J. *J. Alloys Compd.* **2002**, *339*, 90.

(18) Liu, H.; Sullivan, R. M.; Hanson, J. C.; Grey, C. P.; Martin, J. D. *J. Am. Chem. Soc.* **2001**, *123*, 7564.

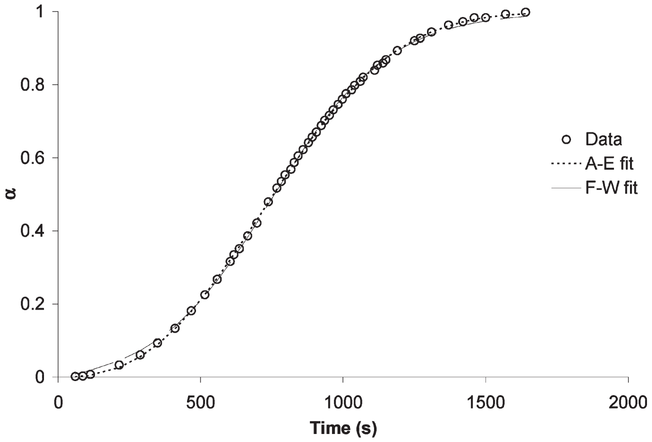

**Figure 4.** Kinetic data for the crystallization of poly(ethylene terephthalate), with fits to the A-E equation (with $n$ = 2.595(9) and $k$=0.00115(1) s$^{-1}$) and to the F-W model (with $k_1$=1.24(3) × 10$^{-4}$ s$^{-1}$ and $k_2'$ = 4.74(4) × 10$^{-3}$ s$^{-1}$). The statistics of the fits are given in Table 1.

**Lu and Hay's Crystallization of Poly(ethylene terephthalate).** The crystallization kinetics of poly(ethylene terephthalate) were studied using differential scanning calorimetry and were found to be sigmoidal-like at several different temperatures.[19] The data were linearized and fit to the A-E equation; one data set, taken at 212 °C, gave $n$ = 2.7 and $k$ = 0.00126 s$^{-1}$.

Fitting all of the sigmoidal data to the A-E equation gives the curve shown in Figure 4, with $n$ = 2.595(9) and $k$ = 0.00115(1) s$^{-1}$; fitting the data with the F-W model gives the fit shown in Figure 4 with $k_1$ = 1.24(3)×10$^{-4}$ s$^{-1}$ and $k_2'$ = 4.74(4)×10$^{-3}$ s$^{-1}$. For this system, the A-E fit is statistically significantly better than the F-W model by a factor of 10$^{13}$, Table 1.

**Phase Transition of $Al_{75}Cu_{15}V_{10}$.** In 1991, Holzer and Kelton studied the transition from amorphous to icosahedral $Al_{75}Cu_{15}V_{10}$ at different temperatures using differential scanning calorimetry.[20] Transmission electron microscopy data suggested that the icosahedral nuclei were not distributed homogeneously; this counters the assumption in the A-E model that "germs" (nucleation sites) are randomly distributed. The authors recognized this, and stated that "Any attempt to interpret isothermal transformation data according to [the Avrami model] is, therefore, fundamentally in error."[20] Nevertheless, the kinetics of transformation were sigmoidal and so the authors created a linearized ln−ln plot using data from 0.2 ≤ α ≤ 0.8. Over the range of temperatures studied, they obtained an average $n$ of 2.3(2); values of $k$ were not given.

We chose one data set, for a phase transition measured at 442 °C, and fit the linearized data to see what $n$ and $k$ values resulted. We compared the resulting parameters, $n$ = 2.2 and $k$ = 1.77 min$^{-1}$, to those we obtained from fitting the entire data set to the A-E equation, $n$ = 1.74(2) and $k$ = 2.02(6) min$^{-1}$, Figure 5. We then fit the entire data set to the F-W model, obtaining rate constants $k_1$ = 0.37(4) min$^{-1}$ and $k_2'$ = 5.4(3) min$^{-1}$, Figure 5. The statistics of the fits, Table 1, show that the A-E and F-W fits are of essentially equal quality, with the A-E equation preferred by a small factor of just 41.

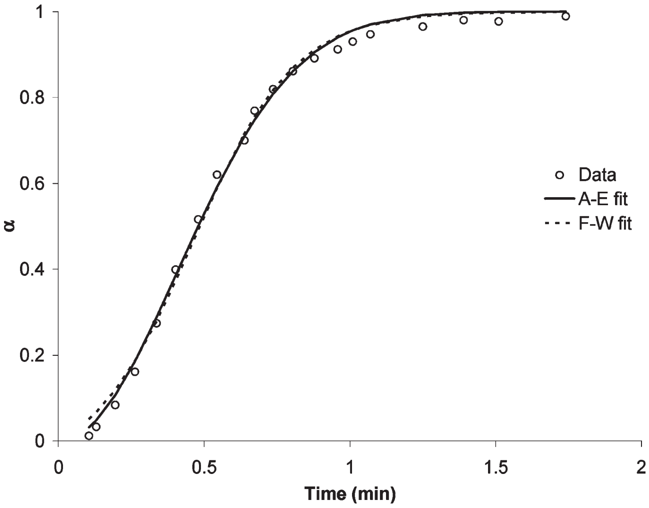

**Figure 5.** Kinetic data for the solid-state transition of amorphous to icosahedral $Al_{75}Cu_{15}V_{10}$ at 442 °C with fits to the A-E equation (with $n$ = 1.74(2) and $k$ = 2.02(6) min$^{-1}$) and to the F-W model (with $k_1$ = 0.37(4) min$^{-1}$ and $k_2'$ = 5.4(3) min$^{-1}$). The statistics of the fits are given in Table 1.

**Crystallization of Glassy $Fe_{80}B_{20}$.** The effects of crystallization on the magnetic properties of iron-based glasses were studied by Greer in 1982, in particular the glassy $Fe_{80}B_{20}$.[21] Using differential scanning calorimetry, Greer obtained the kinetic data shown in Figure 6. Using a linearized ln−ln plot of the data from ∼0.2 ≤ α ≤ ∼0.9, he obtained $n$ = 2.80(5). Again, the value of $k$ was not reported, so we fit the same linear data and obtained $k$ = 0.057 min$^{-1}$.

Fitting the entire data set to the A-E equation gave $n$ = 2.771(9) and $k$ = 0.05726(5) min$^{-1}$, Figure 6, in close agreement with the values from the linearized plot. Fitting the same data to the F-W model gave $k_1$ = 4.8(1) × 10$^{-3}$ min$^{-1}$ and $k_2'$ = 0.257(3) min$^{-1}$, Figure 6. Although the two models give very similar visual fits and $R^2$ values, the AICc statistics suggest that the A-E equation is favored by a factor of 10$^{15}$, Table 1.

**Crystallization of $Pd_{79}Cu_6Si_{10}P_5$ Bulk Metallic Glass.** Very recently, Liu et al. have studied the crystallization kinetics of $Pd_{79}Cu_6Si_{10}P_5$, which has a high glass-forming ability.[22] Using differential scanning calorimetry, the authors obtained kinetic curves for crystallizations at different temperatures; at each temperature studied, the kinetics were sigmoidal. The authors used a linearized ln−ln plot, taking data from 0.15 ≤ α ≤ 0.85 where the data are linear, to determine values for the A-E parameters. For one crystallization at 375 °C, they obtained $n$ = 2.52 and $k$ = 0.06 min$^{-1}$.

When we fit the entire data set to the A-E equation, we obtained the parameters $n$ = 4.68(4) and $k$ = 0.03573(5) min$^{-1}$, Figure 7. These values vary significantly from those obtained from the linearized data. Fitting the same entire data set to the

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(19) Lu, X. F.; Hay, J. N. *Polymer* **2001**, *42*, 9423.
(20) Holzer, J. C.; Kelton, K. F. *Acta Metall. Mater.* **1991**, *39*, 1833.
(21) Greer, A. L. *Acta Metall.* **1982**, *30*, 171.
(22) Liu, L.; Zhao, X.; Ma, C.; Zhang, T. Intermetallics **2009**, in press.

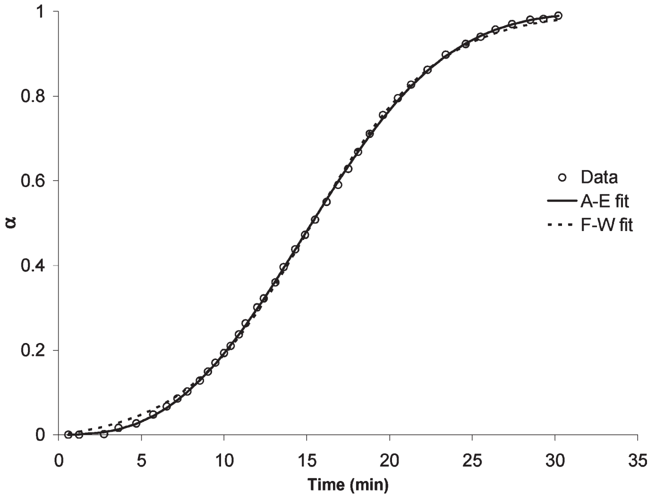

**Figure 6.** Kinetic data for the crystallization of $Fe_{80}B_{20}$ with fits to the A-E equation (with 2.771(9) and $k = 0.05726(5)$ min$^{-1}$) and to the F-W model (with $k_1 = 4.8(1) \times 10^{-3}$ min$^{-1}$ and $k_2' = 0.257(3)$ min $^{-1}$). The statistics of the fits are given in Table 1.

F-W model gave the rate constants $k_1 = 2.7(2)\times 10^7$ min$^{-1}$ and $k_2' = 0.268(4)$ min$^{-1}$, Figure 7. The statistics of the fits show a preference for the A-E equation by a factor of $\sim 10^8$, Table 1, although visually the fits are again very similar.

Summarizing the data in Table 1, we observe that the A-E equation is favored by a significant amount (as defined by an ER$_{(A\text{-}E/F\text{-}W)} \geq 10^{\pm 4}$) for two of the systems, the F-W model is strongly favored for one of the systems, and both models fit equally well (i.e., ER values under the for the $\geq 10^{\pm 4}$) for the remaining three systems. If one examines the statistics in Table S2 in the Supporting Information for the other five data sets that were also randomly selected from the literature and fit, the overall results are as follows: the A-E equation is statistically preferred by a significant amount in three cases (with ER values ranging from $10^8$ to $10^{15}$), the F-W model is statistically preferred in two cases (by ER values of $10^{-14}$ to $10^{-16}$), and the fits are equivalent within experimental error (by the ER of $10^{\pm 4}$ criteria) in the other seven cases. The actual ER values for the fits deemed "equivalent within experimental error" are 0.37, 1.1, 2.5, 41, 52, 588, and 4554, values obviously small compared to the extremes of $10^{\pm 15}$ or more seen above, and especially small compared to the ER values of $10^{-38}$ to $10^{-184}$ seen elsewhere where a four-step version of the F-W model that includes two type of agglomeration reactions provides much better fits in comparison to "dispersive kinetics" models (in that case, however, of different "4-step" type of kinetic data).[11]

In short, the above data along with that in the Supporting Information suggest that it is reasonable to probe further the hypothesis that the A-E and F-W models are somehow equivalent in at least 8 of the 12 cases examined for fitting solid-state kinetic data. Put another way, it would appear to be appropriate to probe further whether or not the chemical-mechanism-based concepts and words from the F-W two-step mechanism, specifically nucleation and autocatalytic growth, are reasonable concepts for describing solid-state processes where good fits to the observed kinetics can be obtained by the F-W model. The driving force for doing so—that is, the goal here—is to overcome the *disconnect currently between the observed kinetics versus the concepts*[11] *and words* employed in the highly complex area[23] of solid-state kinetics. Indeed, we have argued elsewhere that it is this disconnect between at least some of the mathematical-based models that hold questionable physical reality, versus the language that is then adopted from other areas (i.e., must be adopted since no other physical descriptors are available), that has contributed to much of the confusion in solid-state kinetics.[11] As a prime example witness the widespread use in the solid-state kinetics literature of the descriptors "nucleation" and "growth" alongside the A-E equation, *despite the A-E treatment having only one rate parameter, k,* incorrectly typically called a rate constant (which it rigorously is not, since rate constants are defined only via the balanced equations to which they refer; instead, $k$ is a rate-related parameter). It is this specific disconnect (one "$k$" versus two words being used, nucleation and growth) that originally attracted us to try to fit

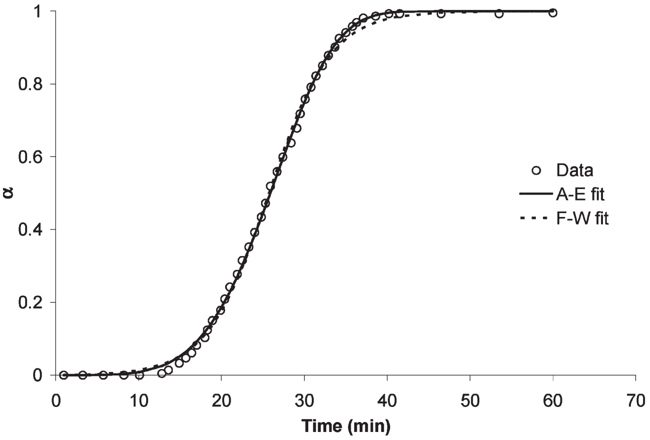

**Figure 7.** Kinetic data for the crystallization of $Pd_{79}Cu_6Si_{10}P_5$ at 375 °C with fits to the A-E equation (with 4.68(4) and $k = 0.03573(5)$ min$^{-1}$) and to the F-W model (with $2.7(2) \times 10^{-4}$ min$^{-1}$ and $k_2' = 0.268(4)$ min$^{-1}$). The statistics of the fits are given in Table 1.

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(23) (a) We wish not to commit the much-discussed sin[10b,23b] of using a concentration, reaction-order based mechanistic model to infer possible insights into complex solid-state processes *without properly stating the caveats involved.* Specifically, one needs to recognize that solid-state reactions have *many complexities not present in typical solution reactions*:[9,10b,23b] spatially constrained reactants, inhomogeneities in reactant distribution; surface area and particle size effects; geometric, preferred orientation, interfacial, and mass- and heat-transfer limitations and effects; and other documented complexities dependent on the history of the sample.[10b] In short, we have no illusions that the observations and resultant hypotheses in the present paper will provide a panacea for all that ails solid-state kinetics. We do hope, however, that the present work will trigger new ideas and possibly new approaches by kinetics experts in the solid-state and thermal analysis communities.(b) Sesták, J. *J. Therm. Anal.* **1979**, *16*, 503–520. In particular, the "sin" we refer to is Sesták's (p 516): "I do hope never to read again introductory sentences such as "solid-state process may be represented by a simplified kinetic relation defined by reaction order...". The point to be grasped here is that since concentration loses its meaning in solid-state kinetics, so does the concept of (concentration-change-determined) kinetic order in the starting material of the phase change (and at least in the absence of clever ways to change the amount of starting material via, for example, fully mixed solid solution type systems (or change the surface area of very intimately mixed solids in some "homogeneous, continuous" way, etc.). This, alone, tells one how different and more complex it is going to be to understand the kinetics and mechanism of solid-state processes .

solid-state kinetics via the chemical-mechanism-based F-W two-step model. *This is not a trivial point.* This disconnect has led for example to concepts such as "autocatalytic nucleation", which is generally defined as the process by which nuclei appear within a matrix as the matrix ages or precipitates.[24] The autocatalytic nucleation mechanism is an assumption made in the solid-state literature; in light of the present comparison between the A-E and F-W models, a reasonable hypothesis (for example) is that the "autocatalytic nucleation" mechanism might be better thought of as continuous nucleation[25] followed by autocatalytic growth. Importantly, we will see in a moment that it is possible to view the A-E parameters $k$ and $n$ as convolutions containing the chemical-reaction-based $k_1$ (nucleation) and $k_2'$ (autocatalytic growth) of the F-W model.

**Fitting Solution Nanocluster Formation Kinetic Data by Both A-E and the F-W Models.** We also hypothesized that data for the formation of $Ir^0_{\sim 300}$ nanoclusters prepared from the reduction of $(Bu_4N)_5Na_3[(1,5\text{-Cod})Ir\cdot P_2W_{15}Nb_3O_{62}]$ that were well-fit originally by the F-W model[5] *could be equally well-fit by the A-E equation.* One such fit, which fully supports the above hypothesis, is also given in the Supporting Information, Figure S6, the resulting AICc ER values favoring the A-E model for the one kinetic curve examined. In short, both the A-E and F-W models are able to fit the variety of phase-transformation kinetic data examined herein, be it solid-state or solution nanocluster formation kinetic data.

**Mathematically Equating the A-E Equation with the F-W Mechanism: Can the Avrami Parameters $k$ and $n$ Be Viewed as Convolutions of $k_1$ and $k_2'$?** Because the A-E and F-W models fit 8 of the 12 sigmoidal kinetic data tested similarly well, we looked at the A-E equation and the integrated rate equation for the F-W mechanism to see how the two models might be related mathematically. Restated, we explored the question of "can one learn anything of value by mathematically equating the two equations?".

To compare the two equations mathematically, we rearranged the F-W integrated rate equation into a form that is directly comparable to the A-E equation. Starting with the integrated rate equation in terms of α, eq 3,

$$\alpha = 1 - \frac{k_1 + k_2'}{k_2' + k_1 e^{(k_1 + k_2')t}} \tag{3}$$

and rearranging eq 3 gives eq 8:

$$1 - \alpha = \frac{k_1 + k_2'}{k_2' + k_1 e^{(k_1 + k_2')t}} \tag{8}$$

The A-E equation, eq 1, is reproduced below

$$\ln(1-\alpha) = -(kt)^n \tag{1}$$

and can be rearranged to the form shown in eq 9.

$$1 - \alpha = \frac{1}{e^{(kt)^n}} \tag{9}$$

We then set eqs 8 and 9 equal to each other, thereby obtaining eq 10, again all in the spirit of a "mathematical gedanken experiment" just to see what resulted and if it is of use or not.[26] Initial inspection of the resultant eq 10 quickly reveals one (albeit not particularly interesting) case where the left (F-W) and right (A-E) sides of eq 10 become identical, namely, that of $n = 1$ and $k_1 \gg k_2'$; see eq S8 of the Supporting Information for further details.[26]

$$\frac{k_1 + k_2^{'}}{k_2^{'} + k_1 e^{(k_1 + k_2^{'})t}} \approx \frac{1}{e^{(kt)^n}} \tag{10}$$

More interestingly, eq 10 can be rearranged to isolate each of the parameters $k$ and $n$ (see the Supporting Information for the attempts to also isolate $k_1$, and $k_2'$). Isolation of $k$ and $n$ is straightforward, resulting in eqs 11a and 11b. Note that in each case a single parameter (i.e., $k$ and $n$ for eqs 11a and 11b, respectively and to start) is a function of the other *three* parameters; for example, $k$ is a $f(k_1, k_2'$, and $n)$ as well as time, t, while $n$ is a $f(k_1, k_2'$, and $k)$ as well as $t$ as expected based on eq 10. More significantly and from a F-W perspective, eqs 11a and 11b reveal more clearly than eq 10 *that nucleation* ($k_1$) *and autocatalytic growth* ($k_2'$) *rate constants are deeply convoluted into both of the A-E parameters n and k,* if one accepts the premise behind the math of equating the two equations in the first place to see what one sees. To our knowledge, *this is the first time where an interpretation for the A-E parameters k and n has been offered in terms of a chemical-mechanism-based equation* and its associated integrated

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(24) Somasundaran, P., Ed. *Encyclopedia of Surface and Colloid Science*, 2nd ed.; CRC Press: New York, 2006; pp 4249−4250. The confusion of "autocatalysis" with the "nucleation" step is apparent in Prout-Tompkins treatments as discussed in Flanagan's lucid review.[4e] Note that the equation defining the nucleation rate (eq 32 elsewhere,[4e] $dN/dt = k_N N_0 + (k_B - k_T)N$) does not have a form consistent with the rigorous kinetic definition of autocatalysis (i.e., $A + B \rightarrow 2B$; $-dA/dt = k[A][B]$), illustrating one example of an insidious disconnect between the kinetics and the words/concepts used to discuss those kinetics.

(25) (a) Let us define what we mean by "continuous nucleation". We mean the process by which many single nucleation events occur over a period of time to achieve *average* nucleation. This is the process measured by the composite (vide infra) nucleation rate constant $k_1$. The use of the term "continuous" nucleations historically served to distinguish the F-W models from LaMer's nucleation and growth mechanism, in which a hypothesized "burst nucleation" takes place in LaMer's scheme due to an essentially infinite nucleation rate. (b) LaMer, V. K.; Dinegar, R. H. *J. Am. Chem. Soc.* **1950**, *72*, 4847.

(26) As further detailed in the Supporting Information, one way to make eq 9 valid is by neglecting the growth step, that is, setting $k_2' = 0$, and by setting $n = 1$. Setting $n = 1$ is analogous to assuming a first-order kinetic process (or, in terms of the KJMA theory, having a one-dimensional phase transition). The resulting equation is then $(1 - \alpha) = e^{-kt}$, where the Avrami $k$ is then equal to the F-W $k_1$. (This case is also known as the Mampel first-order model as discussed by Flanagan on p 17327 elsewhere.[4e]) The result is consistent with the nucleation step (only) of the F-W model being present. While mathematically these assumptions result in the equality between the F-W model and the A-E equation, this limiting case is of little value in treating what the literature denotes as higher-dimension phase transitions.

rate equation and rate constants and where experimental data for equivalent (to sometimes better) fits using the chemical model have also been demonstrated. As such, the above treatment suggests that *it may well be at best confusing, and at worst probably simply wrong—a highly misleading disconnect—to use the words "nucleation and growth" while discussing either of the k or n parameters of the A-E equation.*

$$k \approx \frac{\left\{\ln\left[\frac{k_2' + k_1 e^{(k_1 + k_2')t}}{k_1 + k_2'}\right]\right\}^{1/n}}{t} \tag{11a}$$

$$n \approx \frac{\ln\left\{\ln\left[\frac{k_2' + k_1 e^{(k_1 + k_2')t}}{k_1 + k_2'}\right]\right\}}{\ln(kt)} \tag{11b}$$

Attempts to do the opposite, that is, to rearrange eq 10 to isolate $k_1$ and $k_2'$ in terms of $k$ and $n$, either by hand or using Mathematica, failed in the case of the attempted isolation of $k_1$ and gave a complicated formula in the case of $k_2'$ as eq S9 of the Supporting Information details.

A bottom line here is that eqs 11a and 11b would appear to be of value primarily in suggesting an interpretation in which there is a convolution of one parameter in terms of the other three in each case for $k$, $n$, $k_1$, $k_2$, and time, $t$. Equations 11a and 11b give a specific hypothesis for how $k$ or $n$ may be dependent on $k_1$ and $k_2'$ as well as the other A-E variable (i.e., $n$ or k) and t—at least under the original postulate that the A-E and F-W could be equated in the first place and that doing so might reveal something useful. The reader will need to be the judge here of whether anything useful has resulted.

**Simulations Relating the A-E *n* and *k* to the F-W $k_1$ and $k_2'$.** Our intuition was that we might be able to obtain a clearer, simpler insight in to the relationship between the A-E parameters and the F-W rate constants, so we approached this by simulating kinetic data using the A-E equation, eq 1, for selected values of $k$ and $n$ (selected to give "representative" sigmoidal curves as in Figure 8, for example), and we then fit those simulated data to the F-W kinetic model, eq 3, as described in the Experimental Section to obtain resultant $k_1$ and $k_2'$ rate constants. An example of this simulated data, for $n$ = 3 and $k$ = 0.1, is shown in Figure 8. An immediate conclusion from Figure 8 is that, again, the F-W equation is able to account rather well for A-E type (or in this case, A-E generated) sigmoidal kinetic curves such as the one in Figure 8.

Next, and en route to plots of $k_1$ and $k_2'$ as a function of $k$ and $n$, we independently changed $n$ and $k$ (i.e., one variable at a time, while holding the other constant) and fit the resultant data to the F-W mechanism, eq 3, to see how those $n$ and $k$ changes affect $k_1$ and $k_2'$. The $k_1$ and $k_2'$ versus $k$ plots and the $k_1$ and $k_2'$ versus $n$ plots, Figure 9, are interesting and proved surprisingly simple in light of the apparent complexity of eqs 11a and 11b.

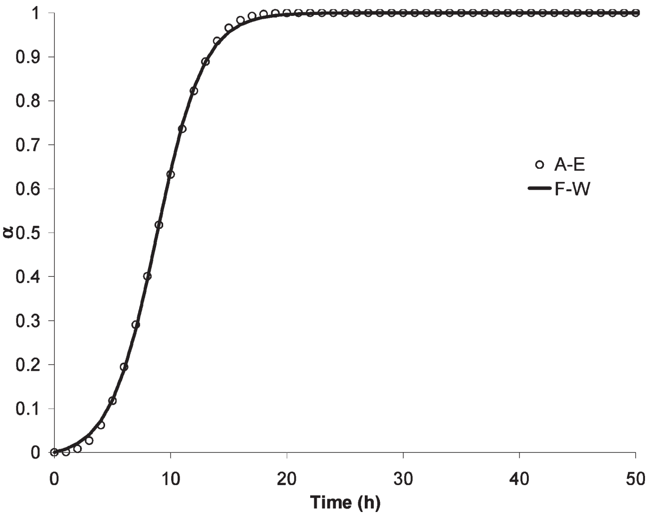

**Figure 8.** Simulated data using the A-E equation (circles) for the parameters $k$ = 0.1 and $n$ = 3, and the fit to the F-W mechanism, eq 3 (line), resulting in $k_1 = 6.1 \times 10^{-3}$ h$^{-1}$ and $k_2' = 0.49$ h$^{-1}$.

As a check on the relatively simple results in Figure 9 versus the apparent complexity of eqs 11a and 11b, several of the data contained in Figure 9 were plugged back into the appropriate eq 11a or 11b for different values of time, $t$, and the resultant right- and left-hand sides of the equation used did in fact give the same numerical value within experimental error, showing, interestingly, that $k$ and $n$ are approximately constant functions of time (i.e., for the specific, limited range of $k_1$ and $k_2'$ values that were investigated, specifically those that provide sigmoidal kinetic curves). That is, the simple linear relationships in Figure 9a,b are actually contained within eqs 11a and 11b, a key here being *for the specific range of n and k values examined.* The interesting, more complete plots of $n$ and $k$ versus $t$ which results from eqs 11a and 11b are provided in the Supporting Information as Figure S7 and show that the values of $n$ and $k$ found from these plots are consistent with the values obtained from the simulations.

Several observations from Figure 9 are worth noting. First, each of the F-W rate constants $k_1$ and $k_2'$ appears to increase linearly with the Avrami rate constant $k$ (and for this constant, $n = 3$, case). The value of $k_1$ has an inverse exponential dependence on $n$, at least for constant $k = 0.1$.[27] The dependence of $k_2'$ on $n$ is more complex. At $n > 1$ (which is almost always the case in the literature), $k_2'$ has a linear dependence on $n$ (at constant $k = 0.1$). When $n = 1$, $k_2' = 0$, since the result is a first-order reaction (with rate equation $\alpha = 1 - e^{-kt}$), and $k = k_1$. When $n < 1$, $k_2'$ is negative, and $k_2'$ decreases rapidly as $n$ approaches zero (see the Supporting Information, Figure S8, for a plot of $k_2'$ versus $n$ for $0 < n \leq 1$). When $n = 0$, then the A-E equation becomes $\alpha = 1 - e^{-1} = 0.632$; that is, $\alpha$ has a constant value for all $t$ in this nonsensical case. It is thought in the solid-state literature that changes in the Avrami exponent $n$ are due to the change in mechanism

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(27) For the simulations with changing $n$, it must be remembered that in general $n$ is between 2 and 4 (although values of $n > 4$ are rare but not unheard of; e.g., see Figures S4 and S5 of the Supporting Information). Hence, nonphysical values of $n$ up to 25 used in the simulations are of use only in establishing the general trends seen by going to such higher $n$ values.

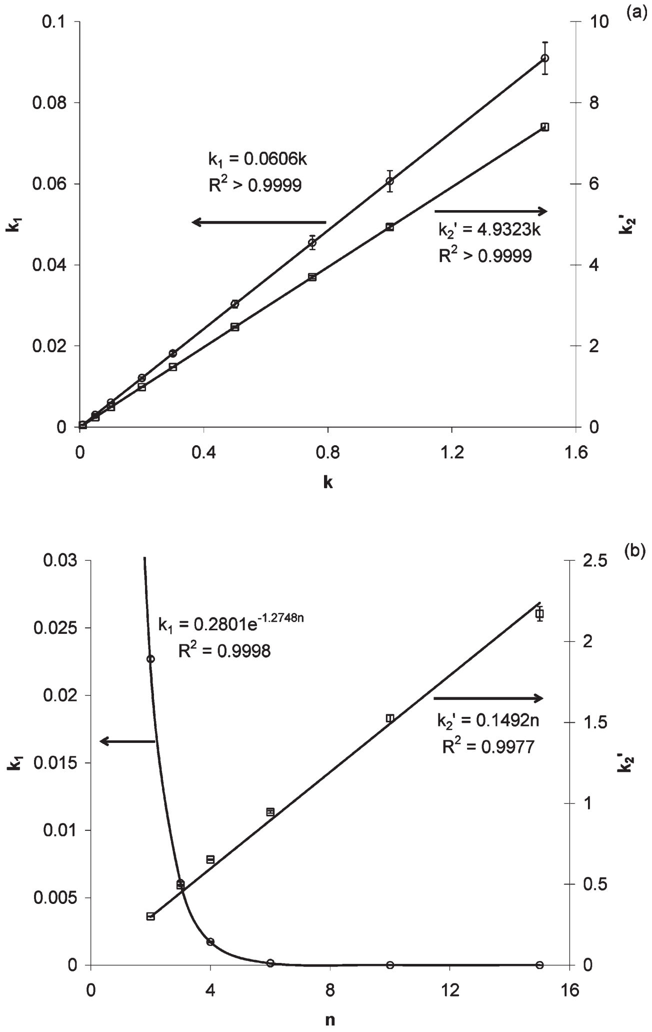

**Figure 9.** Dependence of the F-W rate constants $k_1$ and $k_2'$, obtained from fitting simulated α vs t data for the A-E equation and varying the parameters $k$ (with a constant $n = 3$, (a)) and $n$ (with a constant $k = 0.1$, (b)). In (b), only $n$ values of greater than 1 are plotted (results for $0 < n \leq 1$ are given in Figure S8 of the Supporting Information).

during the course of the reaction;[28] *the present treatment suggests an alternative hypothesis: that the real change simply entails going from predominantly nucleation to predominantly growth, the* $k_1$ versus $k_2'$ *(and t) contributions to n changing as the reaction progresses.*

Overall, this simulation-then-fit approach again makes it quite apparent—but now graphically—that there is a convolution of the F-W rate constants $k_1$ and $k_2'$ into the A-E parameters $n$ and $k$ (or, if one likes, a convolution of the A-E $k$ and $n$ into the F-W $k_1$ and $k_2$), again at least to the extent that equating the two equations makes sense and is justified by the experimental observation of the equally competent fits by the two models in 8 of the 12 data sets examined. The present chemical-mechanism-based approach behind the F-W treatment provides evidence for the inherent physical/chemical disconnect between the A-E model and the underlying chemistry, specifically the F-W model suggests that discussing "nucleation" and/or "growth" from an A-E obtained rate parameter, $k$, is at best bound to generate confusion (witness the concept "autocatalytic nucleation", vide supra) and very possibly may be fundamentally flawed.

A caveat here is that the simulations leading to the above conclusion are just those we have done and found most interesting to date. Obviously, other simulations with a different range of $n$ and $k$ parameters is possible, although our intuition at present is that the initial, broad conclusions made above are not likely to be changed by additional simulations *if* sigmoidal-shaped curves are involved.[29]

**Does Autocatalysis Make Sense for Such Solid-State Phase Transformations?** A Important question, one we thank Prof. James Martin for emphasizing to us, is whether it makes physical sense to use the term autocatalysis for solid-state reactions. While certainly debatable, three points come to mind here to say that it does: (i) certainly the word "autocatalysis" has been often and widely used in the solid-state kinetics literature[3,4,30] (see also the other reviews and references cited in the Supporting Information), albeit not always with the type of experimental support provided herein, and second (ii) at least phenomenologically, to the extent that the F-W model and its autocatalytic second step fit the data, the use of the term "autocatalysis" in the growth step is, therefore, experimentally supported (but *not* terms one can find in the solid-state literature such as "autocatalytic nucleation"). Third, (iii) the idea of an advancing front or interface boundary in the growth of a solid after nucleation is intuitively autocatalytic to at least us in the sense of the rigorous definition of autocatalysis, where the product is also a reactant (i.e., $A + B \rightarrow 2B$ being the rigorous chemical definition of autocatalysis). In short, at least in our view the term "autocatalysis" now has both experimental support as well as past history and usage in the solid-state kinetics literature.

**Comments on the Strengths and Weaknesses of Each Model.** What follows is a brief discussion of the strengths and weaknesses of both the A-E and the F-W models. A more detailed discussion of each, as well as more background information on both the A-E models and its variants as well as on the F-W model, are provided in the Supporting Information for the interested reader.

The main advantage of the A-E model for fitting solid-state data is that it is well-established in the literature, dating back to 1939 in its earliest version (see Table S1 in the Supporting Information). In addition, as can be seen in Figures 1−7, as well as in the Supporting Information, the A-E model fits sigmoidally shaped kinetic data quite

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(28) Sun, N. X.; Liu, X. D.; Lu, K. *Scr. Mater.* **1996**, *34*, 1201.

(29) Since sigmoidal curves inherently include so-called "acceleratory" and "deceleratory" kinetic curves as labeled in solid-state kinetics, one might expect the present general results and conclusions to extend to those cases. That said, an important hypothesis that remains to be tested in future studies is the applicability (or not) of the F-W model to three other of the four main classes of solid-state kinetics to date, "acceleratory, deceleratory, and order of reaction" models ("sigmoidal" curves as tested herein being the fourth class).[4c]

(30) An excellent reference, which makes apparent the long history of the use of the term "auocatalysis" in the solid-state kinetic literature, is reference 4b, that is: Brown, M. E. *Thermochem. Acta* **1997**, *300*, 93–106.

well, be it data for solid-state reactions or solution nanocluster-formation reactions.

The main weakness of the A-E model is clear: *the difficulty in assigning physical meaning to the parameters $k$ and $n$; note in this context that the original driving force for Khanna and Taylor's proposal of the modified Avrami equation used herein (eq 1) is a need to gain physical insight from the Avrami model and its derivatives.*[1] Another significant weakness is that although $k$ is often called a rate constant, it is not, since it is not defined by a specific chemical equation. Instead, $k$ is a (A-E) rate-related parameter, one that the findings herein suggest can be viewed as a convolution that includes the rate constants for chemically well-defined processes of nucleation and autocatalytic growth. Another issue is the A-E parameter $n$, a parameter generally believed to be related to the dimensionality of nucleation; however, exactly how it relates to dimensionality cannot be easily extracted and is indeed a subject of continuing debate as are nonphysical values ("dimensions" in space) of $n < 1$ or $n \geq 4$.[31,32] The present work provides the hypothesis that $n$ might also be viewed as a convolution of nucleation and autocatalytic growth. Moreover, the visually good fits attained by the F-W model in all 12 cases and the statistically equivalent within experimental error (or better) fits obtained in 8 of the 12 cases do show that nothing that one would call a "dimensionality" is needed to obtain equivalent fits to at least the sigmoidal solid-state kinetic data examined. This is not to say that one would not like to build the concept of dimensionality into more complex solid-state kinetic models (i.e., it is not our intention to turn back the clock 70 years on A-E theory and achievements); we also cannot rule out the argument that a F-W treatment of solid-state kinetic data is fundamentally flawed since it does not, at least presently, specifically take into account the dimensionality that physically it seems should be there. This discussion does, however, raise the interesting question for future work of whether a dimensionality can be extracted somehow from $k_1$ and/or $k_2'$.

Another fundamental weakness of the A-E and related equation-based solid-state literature is the large number of different models used to describe the kinetics of solid-state transformations, as Table S1 of the Supporting Information makes very apparent and as Galwey and Brown's treatise also emphasizes.[4c] An issue with the A-E and related models in Table S1 of the Supporting Information is that some are quite complicated without compelling evidence being available that more complicated models are warranted. Indeed, we have shown in the Supporting Information that the A-E model can fit at least some of the data as well as or better than the more complex models used in the literature. Hence, it follows that (i) the use of the simplest models where possible needs to be part of future approaches to solid-state kinetics (i.e., an Ockham's razor based approach that is central tenant of rigorous mechanistic science and was a key to the discovery of the F-W model[5]), and (ii) the use of statistical methods, such as AICc, should be used to provide evidence for or against models with additional parameters. In addition, our results strongly suggest that (iii) linearization of the inherently nonlinear A-E and related equations (e.g., by ln, ln plots) should no longer be done since nonlinear least-squares routines are readily available. No matter what, these three insights would appear to be useful conclusions from the present studies.

Turning to the strengths and weaknesses of the F-W model, the F-W model is a simple, Ockham's-Razor-based mechanism which fits a wide variety of sigmoidal data in nature[5,11−14] closely using only two chemically well-defined rate constants. These rate constants have clear meaning from their chemical-equation basis (at least *in solution*) and can, therefore, be connected rigorously and without confusion to useful chemical concepts/words, notably nucleation ($k_1$) and (autocatalytic) growth ($k_2'$), even if those words and concepts are oversimplifications that may have limitations for complex areas such as solid-state phase transitions.[2−4,9,10,23,42] The F-W model has been able to provide physical insights into at least *solution* nanocluster synthesis and stabilization,[5−7,33] more than 9 insights that include (i) understanding how to form routinely near-monodisperse (defined as ≤±15% size distributions[6]) of typically "magic-number sized" (i.e., full shell) size distributions of supported nanoclusters by the separation of nucleation from growth in time;[6,33] (ii) *rational size control* via a recently developed nanocluster size versus time equation in terms of $k_1$, $k_2$, and the precatalyst concentration, $[A]_0$;[34] (iii) additional possible size control via olefin or other ligand dependence;[35] (iv) rational use of seeded-growth methods including the rational synthesis of all possible geometric isomers of multimetallic "nano-onions";[33a] (v) rational catalyst shape control via ligands capable of attaching to the growing nanocluster faces and thereby preventing autocatalytic surface growth of that facet;[36] (vi) knowledge of the negative effects of, and insights into how to avoid, mass-transfer limitations in nanocluster syntheses;[7] (vii) knowledge of what added nanocluster surface ligands can provide additional nanocluster stability if desired;[37] (viii) a ranking system for nanocluster stabilizers;[38] and (ix) the possibility of nanocluster

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(31) Van Siclen, C. DeW. *Phys. Rev. B* **1996**, *54*, 11845.

(32) Tomellini, M.; Fanfoni, M. *Phys. Rev. B* **1997**, *55*, 14071.

(33) (a) Watzky, M. A.; Finke, R. G. *Chem. Mater.* **1997**, *12*, 3083–3095. (b) Aiken, J. D.III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 9545–9554. (c) Widegren, J. A.; Aiken, J. D.III; Ozkar, S.; Finke, R. G. *Chem. Mater.* **2001**, *13*, 312–324. (d) Hornstein, B. J.; Finke, R. G. *Chem. Mater.* **2004**, *16*, 139–150 see also *Chem. Mater.* **2004**, *16,* 3972–3972 .

(34) Watzky, M. A.; Finney, E. E.; Finke, R. G *J. Am. Chem. Soc.* **2008**, *130*, 11969–11959.

(35) (a) Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335–8353. (b) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891–4910.

(36) (a) Wang, T.; Lee, C.; Schmidt, L. D. *Surf. Sci.* **1985**, *163*, 181–197. (b) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924–1926. (c) Tao, A. R.; Habas, S.; Yang, P. *Small* **2008**, *4*, 310–325.

(37) Ott, L. S.; Finke, R. G. *Coord. Chem. Rev.* **2007**, *251*, 1075–1110.

(38) (a) Özkar, S.; Finke, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 5796. (b) Özkar, S.; Finke, R. G. *Langmuir* **2002**, *18*, 7653. (c) Ott, L. S.; Hornstein, B. J.; Finke, R. G. *Inorg. Chem.* **2006**, *45*, 8382.

size-dependent surface metal-to-ligand bond energies plus all that intriguing preliminary finding implies for catalysis.[7] This list itself would appear to significantly outpace the number of *chemical and physical insights* obtained from 70 years of application of A-E equations,[39] but with the significant caveat here being noted that solid-state kinetic processes are much more complex than are solution processes.[2-4,9,10,23,42]

In addition, a more general 4-step mechanism of nanocluster formation and agglomeration was recently discovered that includes the two steps in Scheme 1 but adds two types of nanocluster agglomeration, bimolecular agglomeration $\mathrm{B} + \mathrm{B} \rightarrow \mathrm{C}$ (rate constant $k_3$) and a novel autocatalytic agglomeration between smaller (B) and larger (C) nanoclusters, $\mathrm{B} + \mathrm{C} \rightarrow 1.5\mathrm{C}$.[7] The latter, four-step mechanism is fortified by the fact that 18 other conceivable mechanisms were ruled out en route to its elucidation.[7] An interesting question related to the present work is if either of the agglomeration steps could have anything to do with phase transformations leading to solid-state products—that is, are there (higher activation energy, slower) solid-state diffusion analogs of the above two steps in the solid state, *especially at higher temperature*? An even more fundamental question is whether greater application of the F-W model to the much more complex area[2-4,9,10,23,42] of solid-state chemistry will help add badly needed physical and chemical insight to solid-state reactions—or will the F-W model prove to be just another model, in the worst scenario an inappropriate model that also commits the apparent sin[23b] of attempting to relate a reaction-order model to solid-state processes. Time will tell.

In terms of *drawbacks* of the F-W model back in Scheme 1, the biggest is surely that this arguably simplest possible, two-step model hides the more intimate mechanistic steps of nucleation and growth in summed, pseudoelementary steps of (average) nucleation and (average) autocatalytic growth.[40] As such the minimalistic F-W kinetic model necessarily conceals the more intimate—formulatable as "dispersive kinetic"[11]—details about the particle formation of phase transformation mechanism, a mechanism in the case of $\mathrm{Ir}^0_{\sim 300}$ nanocluster formation that, logically, must involve $\gg$300 steps for conversion of 300 equiv of $[(1,5\text{-COD})\mathrm{Ir}\cdot\mathrm{P_2W_{15}Nb_3O_{62}}]^{8-}$ into one (on average) $\mathrm{Ir}^0_{\sim 300}$ nanocluster according to the known, balanced stoichiometry in eq 12:[5]

$$300[(1,5\text{-COD})\mathrm{IrP_2W_{15}Nb_3O_{62}}]^{8-} + 750\mathrm{H_2} \longrightarrow$$

$$300$$

$$+ 1\,\mathrm{Ir}^0_{\sim 300} + 300[\mathrm{P_2W_{15}Nb_3O_{62}}]^{9-} + 150\,\mathrm{H}^+ \qquad (12)$$

Hidden by the F-W model is the expectation that nucleation consists of multiple steps leading up to (one assumes) the classical critical nucleus, with dissolution of the cluster being more favorable than growth before the critical nucleus, at least if classical nucleation theory is correct (theory where, however, quantitative agreements between experiment and theory of $10^x$, $x = 1-6$ or more, are common).[41] The nanoclusters grow essentially irreversibly past these initial, again classically reversible steps leading up to the critical nucleus. The rate constants $k_1$ and $k_2$ are therefore *composite* rate constants, *averaged* over all of the nucleation and growth steps, rate constants that change with particle size so that a dispersion of (different) rate constants appears to be present.[11] Those rate contants are, in the oversimplified F-W model, therefore effectively assumed to be independent of nanocluster size, which cannot physically be true at sufficiently high levels of precision. In short, the greatest *strength* of the F-W model, its simplicity and ability to deconvolute an average nucleation rate constant from an average growth rate constant for chemically and physically well-defined nucleation and autocatalytic growth, is also the source of its *greatest weakness*, that simplicity hiding important chemical details that one eventually wants. It follows that possible extensions of the F-W model in the solid state chemistry (or other areas[11-14]) should be carried out with both caution *and* the above limitations clearly in mind.[42]

Work is in progress attempting to elucidate the more intimate steps underlying the F-W model. In the mean time, application of the F-W model is proving to be valuable in deconvoluting an average nucleation rate constant from an average autocatalytic growth rate constant in areas where *this could not done previously*, be they nanocluster formation,[5-7,34,35,37,38] aggregation of proteins intimately involved in neurological diseases,[12-14] or, now, solid-state kinetic data previously treated by the A-E or related equations.

## Conclusions

Herein we have shown the following:

- The A-E equation derived for solid-state kinetics and the F-W mechanism originally worked out for transition-metal nanocluster formation each fit

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(39) A telling testament to this claim is Galwey's and Brown's 1998 treatise:[4c] after being trained in solid-state reactions, then spending 38 years as an expert in the area before retiring in 1997 (see p ix of the preface elsewhere[4c]), Galwey notes in the Preface (p vii) of his and Brown's book[4c] the quote (cited in the main text herein) of "need for greater chemical, rather than mathematical, representations" (of solid-stated reactions and their kinetics). Yet, Chapter 3 of that text presents the many (mathematical) models for solid-state reactions but arguably *very few accepted chemical or physical insights*. His concluding statement, after his 38+ years in the area and the 60+ years at the time of application of A-E and related, typically theory-based equations, is that "In conclusion, a careful balance has to be maintained between the mathematical aspects of modeling and the molecular processes which the models are attempting to represent [99]. Progress in mathematical techniques and theory has far outstripped insights into the controls of reactivity and understanding of the bond redistribution processes involved in crystolysis [89] reactions".

(40) (a) The pseudoelementary step concept, first invented by Richard Noyes for use in treating complex oscillating reactions,[40b-d] involves summing one or more fast reactions with one (to a few) slower reaction(s), giving an overall reaction that can be treated as a (pseudo) elementary step, but which gives kinetic information about the slower reactions. For details about how this is used in nanocluster formation, see elsewhere.[5,7,33d] (b) Noyes, R. M.; Field, R. J. *Acc. Chem. Res.* **1977**, *10*, 214. (c) Noyes, R. M.; Field, R. J. *Acc. Chem. Res.* **1977**, *10*, 273. (d) Field, R. J.; Noyes, R. M. *Nature* **1972**, *237*, 390.

(41) Finney, E. E.; Finke, R. G. *J. Colloid Interface Sci.* **2008**, *317*(2), 351–374 and references cited therein .

either solid-state reaction kinetic or solution nanocluster formation kinetic data equally well within experimental error for 8 of the 12 cases examined. This conclusion is fortified by statistical analysis of the fits in the form of $R^2$ and AICc (and also AICc-based $w$ and ER) values as well as visual comparison of the fits.

- Hence, there is now an experimentally supported way to (i) deconvolute an average nucleation, $k_1$, from an average autocatalytic growth, $k_2$, rate constant from solid-state kinetic data and, importantly, (ii) experimentally supported and rigorously defined words/concepts that can be used to support the discussion of those rate constants, namely, "nucleation" and "autocatalytic growth". These are not trivial results given the history and current confusion in solid-state kinetics[1,4,9,10,39] and the resultant call for more chemical-mechanism-based approaches.[4c,d,9]
- Mathematical analysis, as well as simulations of A-E curves for chosen $k$ and $n$ that yield representative sigmoidal curves, followed by F-W fits of those curves to yield $k_1$ and $k_2'$, reveal that one alternative way to view the A-E parameters $k$ and $n$ are that they are convolutions containing the F-W rate constants $k_1$ and $k_2'$ (as well as $t$ and the other A-E parameter, $n$ or $k$).
- The A-E model has the advantage of its historical use in the literature, but the significant disadvantage that approaching 70 years of its use has not lead to a clear *physical interpretation* of even the two key $n$ and $k$ parameters,[39] at least so far as we can tell and so far as is discernible by an outsider to the field—as basic physical insights should be! Instead, much confusion and a proliferation of more complex models, Table S1 of the Supporting Information, have resulted, all with less and less physical understanding, again that at least we as outsiders can discern.
- The F-W model has the advantage that it employs rigorously chemically defined, physically meaningful rate constants. Its use has allowed more than nine chemical and physical insights into at least solution nanocluster formation and stabilization. The main *limitation* of the F-W model derives from its simplicity: it hides many kinetically important steps and size-dependent properties in average nucleation and average autocatalytic growth, pseudoelementary steps, and their associated rate constants. Other limitations of the F-W model are provided elsewhere that anyone planning to use the F-W model should consult.[33]
- Both the A-E and the F-W kinetic model can fit a variety of solid-state kinetic data from different literature systems, some of which use more complex, yet less physically meaningful, equations. Moreover, the quality of the fits using the F-W mechanism and the A-E equation are in some cases better than the fits to more complex equations used in the specific literature system and by the AICc criterion. *Greater use of AICc statistical methods in the solid-state kinetics area is warranted according to these results*, especially for evaluating models with different numbers of parameters and thus of different complexities.
- A-E type analyses have been shown to generally fit sigmoidal-like kinetic curves for 13 other biological processes[43] ranging from various growth curves (e.g., bacterial growth, sunflower growth, or salamander leg regrowth), $K^+$ conductance in nerve axions or $K^+$ leakage from poisoned muscle, and firefly flash light decay to green leaf IR phosphorescence decay. Since it was shown herein that the F-W model gives equivalent fits to those fits obtained using the A-E model in at least a number of cases, it follows that the F-W two-step model should also fit the above-noted 13 biological processes. An example of the F-W and A-E models fitting biological data is given in the Supporting Information, Figure S11.

Much remains to be done, however. Topics needing attention include the fact that volumes of crystal growth that could range from 10 nm$^3$ to 10 $\mu$m$^3$ or more are obscured by the "fraction reaction" $\alpha$ in both the A-E and F-W treatments herein;[44] the need to analyze more literature data using the F-W model (as well as just the basic, A-E model) to probe for either the generality of the nucleation-plus-autocatalytic-growth model *or its limitations*; the need for efforts aimed at breaking the F-W two-step model into a greater number of its underlying, intimate steps; and the need to address the lack of important concepts from the solid-state literature that are missing in the present version of the basic F-W model, notably the dimensionality, $n$—is $n$ somehow built into, and thus deconvolutable out of, $k_1$ and/or $k_2'$? Or, is the F-W model ultimately inappropriate for analyzing solid-state kinetic data solely based on the fact that it has no dimensionality component and if one cannot eventually be teased out of $k_1$ and/or $k_2'$?

Also unanswered at present is the central question of whether the present discovery will help reduce the confusion and lead to advances in the complex area of solid-state kinetics—or just add to that confusion.[9,10,23] Overall, our hope is that the latter will not happen but, rather,

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(42) (a) One additional specific point here: Garn[42b] points out that the use of an Eyring analysis for temperature-dependent rate constants (e.g., such as would result from use of the F-W model) may prove inaccurate since this analysis relies on molecular vibrations which are suppressed in the solid state. Before anyone would try to extend the present treatment to non-isothermal kinetics (e.g, by the expression of $k_1$ and $k_2$ in terms of an Arrhenius treatment for each rate constant), one should read Galwey[9] and Brown[10b] at a minimum. (b) Garn, P. D. *J. Therm. Anal.* **1975**, *7*, 475.

(43) Cope, F. W. *Physiol. Chem. Phys.* **1977**, *9*, 443–459.

(44) We thank Prof. James Martin for this point. Analogous to what is done with the A-E model, one can set $\alpha=(V-V_0)/(V_m-V_0)$ where $V$ is the crystal volume, $V_0$ is the initial crystal volume (usually zero), and $V_m$ is the maximal crystal volume attained after crystallization is complete.[1d]

that the present contribution will stimulate the needed additional research en route to a better understanding of the kinetics and mechanisms of phase transitions, not just in solid-state chemistry, but also throughout nature. Again, time will tell.

**Acknowledgment.** Multiple, valuable discussions with Professor James Martin about solid-state kinetics and the ideas presented herein are a pleasure to acknowledge, thanks that are not meant to imply that he agrees with the contents of the present paper. In addition, we thank Joe Mondloch and Aimee Morris for their generous critical reading, comments, and equation-checking assistance as we worked through multiple drafts of this paper over a 5 year period that began in 2003. Dr. Pete Skrdla is also thanked for re-emphasizing references 8b−d to us. This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, Grant Number DE-FFD02-03ER15453.

**Supporting Information Available:** A table of selected solid-state literature kinetics studies; fits to five additional literature solid-state kinetics systems to the A-E equation and the F-W model; fits of nanocluster formation data using the F-W and A-E models; an alternate way to relate mathematically the A-E equation and the F-W integrated rate equation; attempts to isolate eq 10 for $k_1$ and $k_2'$; simulations of the A-E parameters $n$ and $k$ as a function of time using eq 10; dependence of $k_2'$ on $n$ for $0 < n \leq 1$; background of the A-E and F-W models; and one representative fit of protein agglomeration data to the F-W and A-E models (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.