A Collision Theory-Based Derivation of Semiempirical Equations for Modeling Dispersive Kinetics and Their Application to a Mixed-Phase Crystal Decomposition

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In recent works, the author has shown the utility of new, semiempirical kinetic model equations for treating dispersive chemical processes ranging from slow (minute/hour time scale) solid-state phase transformations to ultrafast (femtosecond) reactions in the gas phase. These two fundamental models (one for homogeneous/deceleratory sigmoidal conversion kinetics and the other for heterogeneous/acceleratory sigmoidal kinetics; isothermal conditions), based on the assumption of a "*Maxwell*−*Boltzmann-like*" distribution of molecular activation energies, provide a novel, *quantum-based* interpretation of the kinetics. As an extension to previous work, it is shown here that the derivation of these dispersive kinetic equations is supported by classical collision theory (i.e., for gas-phase applications). Furthermore, the successful application of the approach to the kinetic modeling of the solid-state decomposition of a binary system, $CO_2{\bullet}C_2H_2$, is demonstrated. Finally, the models derived appear to explain some of the (solid-state) kinetic data collected using isoconversional techniques such as those often reported in the thermal analysis literature.

Introduction

The author has recently published two novel, *semiempirical* kinetic equations for modeling dispersive kinetics which are based on the assumption of a distribution of activation energies.[1] They have shown great promise in terms of their widespread applicability.[1−4] The equations developed are able to fit and explain even the most challenging asymmetric, isothermal conversion−time ($x - t$) sigmoids, using only two "fit parameters", both of which have units in the time domain. In this work, the application of these equations to the solid-state decomposition of the binary system, $CO_2{\bullet}C_2H_2$ (as studied by Gough[5]), is presented. Additionally, for the first time, an alternate derivation of these equations is provided, starting from assumptions based in collision theory. This derivation is intended to help validate the models, as will be discussed later. The author believes that the approach developed here for modeling dispersive reaction kinetics, based on "quantizing the activation energy barrier", represents a significant advance in the modeling of chemical kinetics.

Background: Kinetic Models for Solid-State Conversions. In the late 1930s/early 1940s, workers such as Johnson and Mehl,[6] Avrami,[7−9] and Erofe'ev[10] discussed crystal physics approaches for modeling solid-state kinetics. The result, the so-called "Avrami equation", which is widely used even to this day for treating nucleation-and-growth-type mechanisms, may be written in differential form as:

$$-\frac{dx}{dt} = kp(1-x)[\ln(1-x)]^{1-(1/p)} \tag{1}$$

where x is the mole fraction of "reagent solids" remaining in the system at time t, and k and p are empirical fit parameters (k is referred to as the rate constant and p is the growth dimensionality). It has been shown that eq 1 may be recast in the following form:[11]

$$-\frac{dx}{dt} = kx^n(1-x)^m \tag{2}$$

which contains the empirical parameters m and n. In sharp contrast to the original derivation, these parameters generally take noninteger values, as opposed to certain ordered integer pairs (e.g., ref 5). The Avrami equation describes the accelerated growth or "branching" of randomly distributed product nuclei, followed by a statistical slowing down of the reaction due to product surface impingement. Written as shown in eq 2, it has a similar form to the basic autocatalytic rate equation, i.e., the Prout−Tompkins (P−T) equation:[2,12−15]

$$-\frac{dx}{dt} = kx(1-x) \tag{3}$$

which generally fits symmetrical $x - t$ sigmoids. The Avrami equation was further generalized with the advent of the Sestak−Berggren (S−B) and extended Prout−Tompkins (EPT) equations.[16,17] The S−B and EPT equations, respectively, can be written as:

$$-\frac{dx}{dt} = kx^n(1-qx)^m[-\ln(1-x)]^p \tag{4}$$

$$-\frac{dx}{dt} = kx^n(1-qx)^m \tag{5}$$

where the empirical fit parameter, q, which is often close to unity, allows the conversion to start (because $dx/dt = 0$ when $x = 0$, the start time of the reaction is inherently undefined; as a result, the "induction period" has historically been a poorly explained feature of sigmoidal $x - t$ curves (e.g., ref 15), until recently.[1,2]). To this day, the Avrami, S−B, and EPT equations continue to be widely used in applications ranging from slurry

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polymorphic transformations of pharmaceutical compounds to solid-state decompositions. Unfortunately, these equations, like other popular solid-state kinetic models (e.g., refs 18−21), are not without shortcomings.[1]

The EPT and S−B models contain the most empirical fit parameters (and in the author's experience, these allow the equations to fit some asymmetric $x - t$ sigmoids): there are four of these in the EPT equation and five in the S−B equation. Taking the EPT equation as an example, one can foresee that small, noninteger differences in m and n (as may often be observed in real experimental data) may make intersystem comparisons of kinetic trends difficult. For example, to directly compare the rate constants, k, or activation energies, E_a, obtained for two different systems, the values of m and n for the two systems being compared should match (within experimental error) to ensure consistency between the conversion mechanisms. Of course, the physical meaning of various numerical combinations of m and n may not be entirely clear with respect to how they relate to particular mechanisms or how they may relate changes in those mechanisms in the first place.

Dispersive Kinetics. Dispersion in the activation energy of a process is often caused by molecular dynamics effects; e.g., molecules in a given ensemble can react at different times simply due to the fact that they have different speeds, path lengths between collisions, collision geometries, etc. This idea represents a fundamental assumption in the area of dispersive kinetics. Dispersion in the activation energy barrier, in turn, creates a distribution of molecular reactivities (i.e., rate constants) that helps to define the kinetics of the conversion taking place on a macroscopic (measurable) scale. Although an activation energy barrier is typically defined on a potential energy surface, the dispersion can be considered to be kinetic in origin as, for example, it may be caused by differences in the molecular speeds of otherwise identical reagent molecules in a given ensemble.

Dispersive kinetics can be observed in all phases of matter provided that the phenomena causing the dispersion occurs on a time scale that is similar to, or slower than, the overall (i.e., macroscopic) conversion rate. Because of the wide range of chemical processes that may potentially fall in this category, the study of dispersive kinetics is of great importance. For this reason, a cursory overview of traditional dispersive kinetic approaches is provided below before the author's own, unique interpretation of these systems (which can be considered to be based on a combination of quantum mechanics and dispersive kinetic theory) is presented. As support for the development of a new approach for modeling solid-state kinetics, the author cites the recent publications by Galwey, who has criticized traditional approaches for treating and explaining thermal kinetic data and has called for reform in this area (e.g., ref 22).

As mentioned earlier, dispersive kinetics are observed when a chemical conversion occurs on a time scale that is comparable to, or shorter than, that of the internal rearrangements (mixing) continuously occurring inside the reacting system.[23] Classical examples of dispersive kinetics are found in the electron transfer in viscous solvents, the reactions of large biomolecules, reactions in glasses, and femtosecond events in fluid media.[24] In these cases, the Arrhenius assumption of a single activation energy fails. Instead, introducing the concept of *fractal time* (which allows for the mathematical treatment of individual molecules in a system reacting on different time scales, e.g., see the Kohlrausch−Williams−Watts (KWW) equation discussed below) to account for molecular dynamic effects (i.e., relaxation[23]), assuming the continuous time random walk (CTRW) model of Montroll and Weiss[25] for the molecular motion, one finds that the rate constant for the chemical conversion is time-dependent (as is the activation energy) and, ultimately, that this time-dependent rate constant may be derived mathematically by starting with a distribution of activation energies for a given dispersive conversion. These are concepts that are common to the various stochastic models of kinetics occurring in "renewing environments", a field which was recently reviewed by Plonka.[23,24]

Fundamentally, the Kohlrausch−Williams−Watts (KWW) relaxation or "stretched exponential" function, ϕ_{KWW}, serves as a starting point for many treatments of dispersive processes. As pointed out by Plonka, while the KWW stretched exponential and Curie−von Schweidler (CvS) power law have been used essentially universally to characterize the relaxation of thousands of systems to date, these remain *phenomenological* (i.e., empirical) formulas.[24] The KWW function has the following form:

$$\phi_{KWW} = \exp[-(t/\tau)^{\alpha}]; \qquad 0 < \alpha \leq 1 \tag{6}$$

where t is the time, τ is the effective relaxation time, and α is the dispersion parameter for relaxation. For first-order dispersive kinetics, one may write:[26]

$$\phi_{KWW} = \int g(k) \exp(-kt)\, dk = \int f(\tau) \exp(-t/\tau)\, d\tau; \quad \text{for } f(\tau) = g(1/\tau)/\tau^2 \tag{7}$$

where k is the (time-dependent) rate constant for the conversion and the integration limits are 0 and ∞ for each of the above equations. The functions $g(k)$ and $f(\tau)$ represent probability density functions for the rate constants and relaxation times, respectively, in a superposition of monoexponential decays (i.e., for the individual molecules in the ensemble reacting on various time scales) that is *approximated* by the KWW function.[27] Taking the inverse Laplace transform of ϕ_{KWW} yields $g(k)$ (or, alternatively, $f(\tau)$). If $g(k)$ is obtainable, one may also determine $g(\epsilon_a)$, the corresponding probability density function for the activation energy of the process, using the relation:[28]

$$g(k) = [-h \exp(\epsilon_a/k_BT)][g(\epsilon_a)] \tag{8}$$

(where k_B is the Boltzmann constant and h is the Planck constant) which is obtainable directly from the Eyring definition of the rate constant:

$$k = (k_BT/h) \exp(-\epsilon_a/k_BT) \tag{9}$$

and the relation:

$$g(k)\, dk = g(\epsilon_a)\, d\epsilon_a \tag{10}$$

Unfortunately, inverse Laplace transforms are known exactly only for α values of $^1/_3$, $^1/_2$, and $^2/_3$. For other cases, the mathematics may be nontrivial and/or the results may be difficult to interpret (e.g., ref 24). Additionally, the inverse Laplace transform becomes an ill-conditioned problem in the presence of noisy data.[29] We highlight here the fact that the Avrami equation, discussed earlier, is a simple result of this "traditional" dispersive kinetic approach, which is obtainable by starting with the KWW function and assuming first-order kinetics.[23,24,26,30] However, the limitations of the Avrami equation are evident from numerous works, including that of Gough,[5] which we will examine later in this paper. As an aside, the nucleation-and-growth theory of Yu[31] has demonstrated much greater generality; the Avrami equation is a result of this theory that is obtained by considering the simplest, homogeneous systems.

A New Direction in the Modeling of Dispersive Reaction Kinetics. While the assumption of a distribution of activation energies has been applied to such diverse areas of study as ion channels (e.g., ref 28) and combustion reactions (e.g., refs 11, 32), the approach is not prevalent in the solid-state kinetics literature. Instead, much of the literature dealing with solid-state phase transformations and decomposition reactions has focused on either “model-free” isoconversional methods (e.g., refs 33−36) or the use of a standard set of kinetic models (e.g., 18−21), or both (e.g., 37), with either isothermal or nonisothermal approaches (e.g., 38). Isoconversional methods have provided the thermal analysis community with a view into the complexity of many solid-state processes, but these approaches unfortunately do not provide much mechanistic insight into the conversions. Interestingly, however, for some elementary phase transformations (e.g. 18, 39), it appears that the activation energy, E_a, obtained as a function of the extent of conversion, x (or $1 - x$), may be adequately described by a single distribution. It is in these cases where the author has recently focused his attention.

Since 2005, the author has attempted to derive new kinetic models that exhibit the following characteristics: mathematical simplicity, ease of use, high-quality fits to experimental data, and physical relevance of the fit parameters (note: it is believed that the latter may be achieved by avoiding the use of phenomenological equations, where possible). The approach taken requires that a *molecular activation* energy distribution be defined a priori with respect to the derivation of the kinetic model(s), which is opposite to the majority of the approaches in the dispersive kinetics literature. As mentioned earlier, this activation energy distribution, $D(\epsilon_a)$, is the result of “system renewal”[1] occurring continuously during the course of the conversion. The Maxwell−Boltzmann (M−B) distribution is selected to define $D(\epsilon_a)$, regardless of the fact that it is typically used to describe the molecular speed/kinetic energy distribution of an ideal gas, as a first approximation. This distribution was chosen because the partition function for molecular motion in an ideal gas has an analytical solution and thus the M−B distribution has an algebraically manageable form. Additionally, the M−B distribution has a desired asymmetric shape (note that many isothermal, solid-state conversions exhibit asymmetric, sigmoidal shapes[1]), unlike a Gaussian distribution that is based on random walk, Brownian motion. The author believes that $D(\epsilon_a)$ is ultimately a convolution of a kinetic energy distribution (which results from molecular dynamics, hence the use of the M−B kinetic energy distribution) and a potential energy (which relates to the classical Arrhenius definition of the activation energy). To summarize, the approach to dispersive kinetics that is described in this work is a simple, statistical mechanical one (perhaps more easily envisioned for gas-phase applications), which does not attempt to rigorously describe various modes of molecular motion occurring in different phases. Note that, while the M−B distribution has previously been dismissed as being inapplicable to solid-state kinetics, based on the fact that solids contain immobilized constituents, Arrhenius kinetics are supported by both Fermi−Dirac (for electrons) and Bose−Einstein (for photons) distributions, which have similar functional forms to the M−B distribution.[40]

Results and Discussion

Semiempirical, “Statistical Kinetic” Model Equations: A Novel Treatment for Dispersive Kinetics. In Eyring’s transition-state theory (TST), reagent molecules collide, in a bimolecular reaction, to form a high-energy “activated complex (AC)” species that defines the activation energy barrier (relative to the zero-point energy). This complex exists in the vicinity of the transition state (TS) on a potential energy surface (PES) in a “pseudo-equilibrium” with both the reagents and products. The decomposition of the AC occurs on the time scale of a low-energy bond vibration, either yielding products or regenerating the reagents.[41] Unfortunately, the direct application of this theory to different reaction mechanisms and to conversions in condensed phases raises key fundamental questions. For example, what is the nature of the AC when one does not have a homogeneous, bimolecular reaction (i.e., for a solid-state phase transformation)? Because the “quantization of the activation energy barrier” in the Eyring case uses relatively high-energy quanta (i.e., bond vibrations), the result is inherently a single activation energy, which, for a given conversion, correlates to a unique (i.e., time-independent) value of the rate constant.

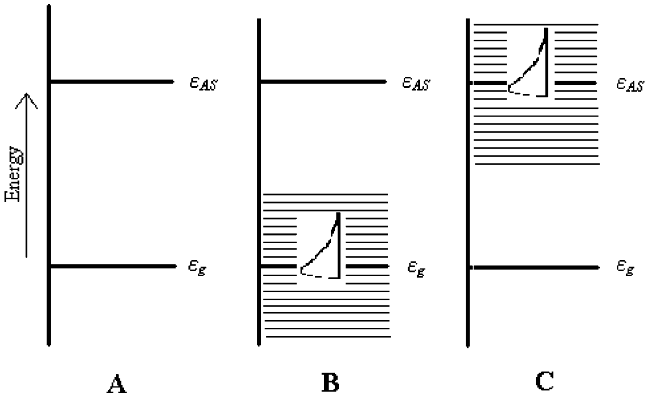

Figure 1. Schematic representation (not drawn to scale) of energy levels that impact the kinetic descriptions of systems with (A) Arrhenius−Eyring kinetics, i.e., a single activation energy, (B) homogeneous (deceleratory) dispersive kinetics, and (C) heterogeneous (acceleratory) dispersive kinetics; see text for details. Energy (both potential and kinetic) increases along the vertical axis. The narrowly spaced energy levels are akin to translational quanta, which are assumed to be populated in accordance with the functional form of the M−B distribution (depicted by the graphic embedded within these energy levels).

In sharp contrast to the work of Eyring, the author has selected to use, as a first approximation, the quantization of a much lower energy (dynamic) property of molecules (translational motion) as a basis for quantizing the activation energy barrier (it is noted here that, for polyatomic molecules, the total kinetic energy contains translational, vibrational, and rotational components, but the latter two typically represent significantly higher energy modes than translational motion). Translational motion is of sufficiently low energy to allow the quantization of typical activation energies (ca. 30−300 kJ/mol) into small, discrete units which, when summed over the population of a reasonably large molecular ensemble, yields a mathematically smooth distribution of states (this is important for mathematical integration, as was discussed previously[1]). However, because the potential energy barrier to conversion can be considered to be unique to each process, in dispersive kinetics, one obtains an activation energy distribution that takes the *shape* of the kinetic energy distribution. In other words, the quantization of the activation energy occurs in the kinetic energy component.

Figure 1 shows a schematic energy diagram outlining what the author believes to be the key differences between the traditional Arrhenius−Eyring definition of the activation energy, ϵ_a (where $\epsilon_a = \epsilon_{AS} - \epsilon_g$) and his definition of $D(\epsilon_a)$, for both acceleratory and deceleratory dispersive processes (note: the energy levels in this schematic pertain to species that define the rate-determining step, rds, of the process, which is assumed to be unchanged over the duration of the conversion). Note that the kinetic energy distributions in Figure 1 would normally be shown inverted if the vertical axis was labeled "potential energy", instead of simply "energy", to reflect the idea that potential energies and kinetic energies are inversely related, as in the classical mechanics sense. For nondispersive processes, the entire reagent population reacts with a single activation energy, as shown in "A" in the figure.

In homogeneous dispersive processes (e.g., solid-state thermal decompositions (e.g., refs 18, 47)), the dispersion in the activation energy originates from kinetic energy differences that are attributable to the *reagent population*. This effect produces *deceleratory*, sigmoidal $x - t$ profiles, in which the reagent molecules with the highest kinetic energies react before the lower kinetic energy molecules (as one may expect). In sharp contrast, for heterogeneous dispersive processes (e.g., crystallizations and solvent-mediated polymorphic transformations (e.g., refs 1, 19)), the dispersion is predominantly attributable to the "*activated state* (AS)" (note: the author's definition of the AS is more generally defined than the AC in TST in that the AS can generally be any species that is higher in potential energy than the starting material). For example, in a crystallization governed by a nucleation-and-growth mechanism, *acceleratory* $x - t$ profiles are often observed experimentally. In such cases, molecules with the lowest kinetic energies react before those with higher kinetic energies. This makes sense in light of the fact that many crystallizations initiate on cold surfaces or with the introduction of seed crystals; these surfaces are believed to "slow the motion of the colliding reagent molecules" so that they can be incorporated into the developing lattice (thus, the crystal lattice represents the higher energy state, i.e., the AS). As the conversion proceeds, more reagent molecules are consumed. The conversion occurs coincidentally with a decrease in the activation energy (i.e., with increasing time), which produces the acceleration in the sigmoidal $x - t$ transient. In general, $D(\epsilon_a) = \epsilon_{AS} + D(\epsilon_{KE})$ for a deceleratory process (labeled "B" in Figure 1), while $D(\epsilon_a) = -D(\epsilon_{KE}) - \epsilon_g$ for an acceleratory process (labeled "C" in Figure 1), where $D(\epsilon_a)$ is the activation energy distribution, as defined earlier, $D(\epsilon_{KE})$ is the energy distribution of the species responsible for the dispersion, and ϵ_g refers to the zero-point energy level of the reagent species for the acceleratory case. Note that, in the case of a deceleratory conversion, ϵ_g is a distribution and thus it is defined simply as $D(\epsilon_{KE})$ in the figure.

Previously, the author assumed an activation energy distribution having the functional form of the M−B distribution or "inverted M−B distribution", depending on whether the solid-state kinetics were heterogeneous (acceleratory) or homogeneous (deceleratory), respectively, in nature[1]. From Figure 1, the origin of the "∪"- and "∩"-shaped $D(\epsilon_a)$ is readily apparent. It is emphasized here that the author hypothesizes that: (1) both molecular-level kinetic energies (e.g., from collision theory) and a potential energy barrier (as per the classical Arrhenius equation, denoted as "$\epsilon_a°$" later in the paper) are essential in the treatment of dispersive reaction kinetics using the approach discussed in this work, and (2) the "M−B-like" kinetic energy distributions assumed in this treatment can be mapped onto a PES for a given reaction using an inverse relationship between the kinetic and potential energies, much like a ball rolling down a hill under the force of gravity converts potential energy into kinetic energy.

First-Order Statistical Kinetic Models for Dispersive Kinetics: Comparison of the Original Derivation to a Collision Theory-Based Derivation. It was previously shown[1] that one can convert the traditional M−B speed distribution[42] to a corresponding kinetic energy distribution and then use the latter distribution, together with the Eyring equation (eq 9), to define the functional form of the corresponding distribution of rate constants. This distribution of rate constants relates a system rate constant, $k(t)$, which has a quadratic dependence on time:

$$k(t) = (2\alpha\beta)\exp(\beta t^2) \quad (11)$$

where α and β are constants (under isothermal conditions). This expression for $k(t)$ can be inserted into the following equation:

$$x = \exp[-\int k(t)\,dt]; \quad \text{integration limits from } t = 0 \text{ to } t = t \quad (12)$$

that describes the kinetics of a process using an integrated first-order equation in which the rate constant is time-dependent[11] and then integrated. The result is a *semiempirical* model equation for treating the *acceleratory/ heterogeneous* dispersive kinetics under isothermal conditions:

$$x = \exp\{[-\alpha/t][\exp(\beta t^2) - 1]\} \quad (13)$$

The derivation of eq 13 was presented in detail elsewhere[1]. Note that the derivation of this equation neglects an explicit description of the potential energy contribution to the activation energy barrier because this energy is a constant and thus it does not affect the *shape* of $D(\epsilon_a)$. Similarly, for *deceleratory/homogeneous* processes, the time-dependent rate constant for the overall conversion can be defined as[1]:

$$k(t) = (2\alpha\beta)\exp(-\beta t^2) \quad (14)$$

By using eq 14 in eq 15 (which assumes a dimensionality of two for the process, hence the t^2 term, which supports the idea of 2-D nucleation/denucleation occurring on predominantly flat crystal faces (e.g., ref 43); in contrast, the dimensionality = 0 for heterogeneous conversions in which the activated state is defined by dissolved molecules, as per eq 12), below,

$$x = \exp[-t^2\int k(t)\,dt] \quad (15)$$

and integrating from $t = 0$ to $t = t$, one obtains the following (isothermal) dispersive kinetic model:

$$x = \exp\{[\alpha t][\exp(-\beta t^2) - 1]\} \quad (16)$$

which has a similar form to eq 13. (Note: even though an approximation is used during the integration that ultimately yields both eqs 13 and 16,[4] it has been shown that these equations remain valid in the modeling of data down to low integer values of t, the units of which can be arbitrarily selected, to begin with.) The fit parameters, α and β, have units of (time) or (time)$^{-1}$ and (time)$^{-2}$, for the deceleratory and acceleratory model equations, respectively; these constants may be referred to as "global rate parameters".

The Arrhenius equation is generally considered to provide a "coarser representation" of the Eyring equation. It can be shown that the Eyring equation yields the same expression as that which can be obtained from collision theory (CT), for a bimolecular reaction of ideal gases.[41] This observation lends a level of "self-consistency" to these fundamental kinetic theories, meaning that, at a very high level, they can essentially be considered identical (i.e., mathematically, in considering the model equations). The derivation that follows attempts to demonstrate a similar "self-consistency" for the semiempirical, dispersive model equations (i.e., eqs 13 and 16) by starting with the CT-based assumption of a molecular speed term in the preexponential factor of the rate constant expression and not explicitly assuming a molecular distribution of activation energies as per the previous derivation[1]. Some of the key outcomes of the earlier derivation are utilized, together with the basic assumptions of CT, to verify that: (1) the "distribution of activation energies" observed experimentally for dispersive processes is kinetic in origin and (2) potential and kinetic energies may be combined, as shown schematically in Figure 1, to treat the kinetics of dispersive processes. In doing so, the goal is to provide the reader with a different perspective of the molecular-level basis for the author's "quantizing of the activation energy barrier" in dispersive kinetics.

CT is based on the assumption that the rate constant for a given conversion is proportional to the product of three terms: a steric term, an encounter rate, and a minimum energy requirement (i.e., the "exponential term").[41] Thus, a general expression for the molecular rate constant, k, may be written as:

$$k = P^*\sigma(8kT/\pi\mu)^{1/2}\exp(-\epsilon_a/k_BT) \qquad (17)$$

for a bimolecular reaction of ideal gases (where P^* is the steric factor, σ is the collision cross-section, μ is the reduced mass of the colliding molecules, and ϵ_a, k_B, and T are defined as before). Neglecting the steric factor, the preexponential term relates the product of the collision cross-section and the relative mean speed of the reacting species. For this reason, one can consider using eq 11 (assuming isothermal conditions) in the preexponential term of eq 17 to describe a distribution of rate constants that originates from the variations in molecular speeds. By doing so, one obtains the equation:

$$k = \Lambda\exp(-\epsilon_a/k_BT)\exp(\beta t^2) \qquad (18)$$

where Λ is a term that encompasses the pertinent (iosthermal) constants of the CT rate expression. Note that, in eq 18, k is a function of both t and T, in contrast to eq 17.

By rewriting eq 18, it is found that:

$$k = \Lambda\exp[(-\epsilon_a + k_BT\beta t^2)/k_BT] \qquad (19)$$

Returning to the schematic in Figure 1, it was observed that, for a dispersive, heterogeneous/acceleratory conversion, the activation energy distribution may be graphically represented by: $D(\epsilon_a) = -D(\epsilon_{KE}) - \epsilon_g$. From eq 19, the corresponding t-dependence of the activation energy, $\epsilon_a(t)$, is given by: $\epsilon_a(t) = \epsilon_a^\circ - k_BT\beta t^2$, where ϵ_a° is the time-independent potential energy barrier to conversion. Conversely, for a homogeneous/deceleratory conversion, it was found that, graphically, $D(\epsilon_a) = \epsilon_{AS} + D(\epsilon_{KE})$; from eq 19, $\epsilon_a(t) = \epsilon_a^\circ + k_BT\beta t^2$ (note that in this case, the net activation energy barrier clearly increases with time, which causes a deceleration in the conversion rate, characteristic of homogeneous conversions). From these results, support is gained for the idea that the activation energy distribution of dispersive processes has both kinetic energy and potential energy components, which can be differentiated based on the fact that the former is time-dependent while the latter is not. Interestingly, the time-dependent activation energy equations derived here have a form that is not unlike that derived by Plonka for a first-order dispersive reaction.[23]

By using eq 19 in eq 12 and integrating from $t = 0$ to $t = t$ (with the aid of the mathematical simplification, as before[4]), one obtains *precisely* eq 13, in which β is defined simply as a constant as before, but:

$$\alpha = \Lambda\exp(-\epsilon_a^\circ/k_BT)/2\beta \qquad (20)$$

Similarly, for the homogeneous/deceleratory case, one obtains eq 16, but, in that case, $\alpha = -\Lambda\exp(-\epsilon_a^\circ/k_BT)/2\beta$. Thus, it is demonstrated that one can use two "orthogonal" derivations to obtain the same two semiempirical model equations. It is highlighted here that eq 20 is an entirely new result, which clearly shows that the *potential energy barrier* to conversion is time-independent and, as a result, it shows up as a component of the α term (the $\Lambda/2\beta$ portion of this term is an expected result from the original derivation[1]) in both model equations, eqs 13 and 16.

By using eq 20, it can also be shown why, in the author's earlier work[1], it was possible to plot $\ln(\alpha\beta)$ vs $1/T$ for the solvent-mediated polymorphic transformation of a pharmaceutical compound, i.e., in a "traditional Arrhenius plot", to obtain an estimate of the "global activation energy" from the slope of the linear regression fit of the data. This is because:

$$\ln(\alpha\beta) = \ln(\Lambda/2) - \epsilon_a^\circ/k_BT = \ln(\Lambda^*) - E_a^\circ/RT \qquad (21)$$

and thus the slope of such a plot is given by "$-E_a^\circ/R$" (where R is the gas constant), as per the Arrhenius equation (the vertical intercept of the line, $\ln(\Lambda^*)$, is also consistent with the Arrhenius equation, where Λ^* is typically called the "frequency factor"; the "$^1/_2$" coefficient may arise from assuming a unimolecular process, whereas Eyring reactions are inherently bimolecular). From eq 21, one can see that the "global activation energy", E_a°, is actually the (molar) time-independent potential energy barrier to the conversion. It is highlighted here that because E_a° is simply a potential energy, yet the kinetic energy contribution to the observed activation energy distribution is a function of t (which is directly related to x, for a known conversion mechanism, at constant T), it should be possible to obtain both E_a° and β for a given conversion by performing isothermal kinetic experiments at different temperatures. This may be of interest since it was shown earlier that, together, E_a° and β define the "time-dependent activation energy", $E_a(t)$ (and, thus, potentially also the "distribution of activation energies" for the conversion; this idea will be pursued in future work), of dispersive kinetic processes.

Treatment of $CO_2{\cdot}C_2H_2 \rightarrow CO_2 + C_2H_2$ Conversion Kinetics Using Semiempirical Dispersive Model Equations. In previous works, it was shown that the kinetic approach described here can be applied to a host of dispersive processes: both heterogeneous and homogeneous (isothermal) solid-state conversions,[1] femtosecond reactions in the gas phase,[4] and even lifespan modeling in animals.[3] As part of this work, an attempt is made to demonstrate yet another application: the decomposition of the *mixed-phase* cryogenic crystals of $CO_2{\cdot}C_2H_2$, as studied by Gough et al.[5] This system is unique even with respect to the diverse array of applications previously studied, as it involves a two-component reaction which is accompanied by a phase change. While the reaction mechanism is clearly first-order (from the chemical equation), one can see from inspection of the $x - t$ trends in Figure 2 that the kinetics are heterogeneous (i.e., acceleratory) in nature, although the system is obviously very different from the slurry polymorphic transformation to which eq 13 was applied previously.[1]

Gough et al. found that the low-temperature solid-state conversion, $CO_2{\cdot}C_2H_2 \rightarrow CO_2 + C_2H_2$, is poorly described by the Avrami equation. However, the $x - t$ plot for this conversion, which is reproduced in Figure 2, was able to be fit through numerical solution, assuming a distribution of polyhedral volumes (interestingly, having the functional form "av^2

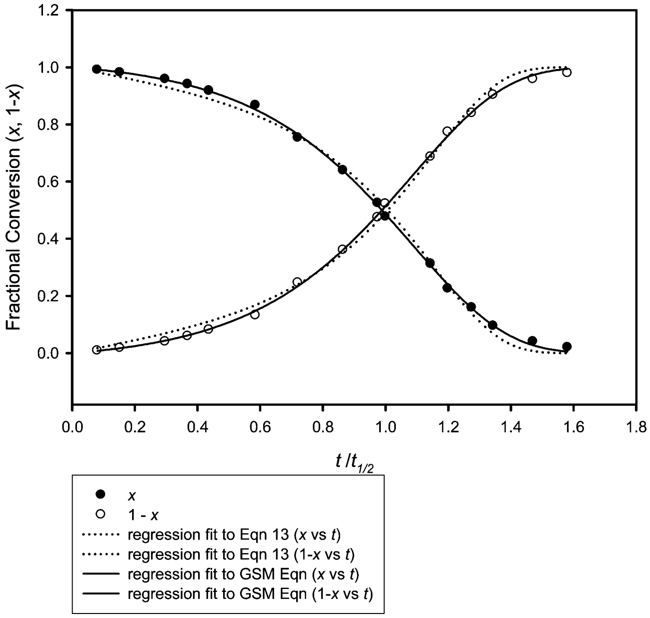

Figure 2. "Conversion vs reduced time" plot for the decomposition of $CO_2{\cdot}C_2H_2$. The data points were extracted from ref 5. The time axis is in units of the half-life of the conversion ($t_{1/2} \sim 1.02 \times 10^4$ s). The broken lines represent regression fits to eq 13: $\alpha = 0.116 \pm 0.014$ s, $\beta = 1.92 \pm 0.09$ s^{-2}. The solid lines represent regression fits to the GSM equation (see text for details): $\alpha = 0.088 \pm 0.004$ s^{-1}, $\beta = 3.35 \pm 0.06$ s^{-1}.

$\exp(-bv^2)$", where a and b are constants and v is the terminal volume of the growing product crystal) and assuming unimpeded growth in three dimensions until the point of complete consumption of local reagent material. From Figure 2, one can see that eq 13 fits the data quite well ($R^2 = 0.996$), supporting the idea that the kinetics are heterogeneous/acceleratory. Conversely, eq 16, for use in homogeneous/deceleratory systems, is unable to fit the data with any degree of precision.

As an aside, it is interesting to point out that the "Gompertz survival model" (GSM), often used in biological applications, does an even better job of fitting the data in the figure ($R^2 = 0.999$) than eq 13. As shown previously,[3] the GSM equation may be written in similar form to eq 13:

$$x = \exp\{[-\alpha/\beta][\exp(\beta t) - 1]\} \tag{22}$$

In fact, the GSM equation may be obtained directly by using the following form of the time-dependent rate constant, $k(t)$:

$$k(t) = \alpha \exp(\beta t) \tag{23}$$

in the integrated form of a simple first-order rate expression having multiple rate constants, i.e., eq 12. Essentially, the only difference between the GSM equation and eq 13 is the order of the time-dependence of $k(t)$ (note: the preexponential term, $2\alpha\beta$, provides a minor simplification to our final result, eq 13).

Conclusions

The intent of this account is to provide the reader with additional insights into the origin of the author's dispersive or "statistical kinetic" semiempirical model equations. Figure 3 summarizes the key findings of this work in the form of a schematic illustration. The author believes that the semiempirical models presented here (eqs 13 and 16) may offer a more physically meaningful approach for the treatment of solid-state kinetic data compared to that of standard (i.e., nondispersive) kinetic models. Some of the advantages of the dispersive kinetic models, over existing kinetic models, may include the high quality of the data fits, the ability to estimate or even define a start time for the conversion, and the use of only two fit parameters, each with physical units. The author hopes that, with broader use, these equations continue to demonstrate versatility in a wide range of chemical applications, simultaneously helping to reaffirm some of the assumptions made in the development of these models.

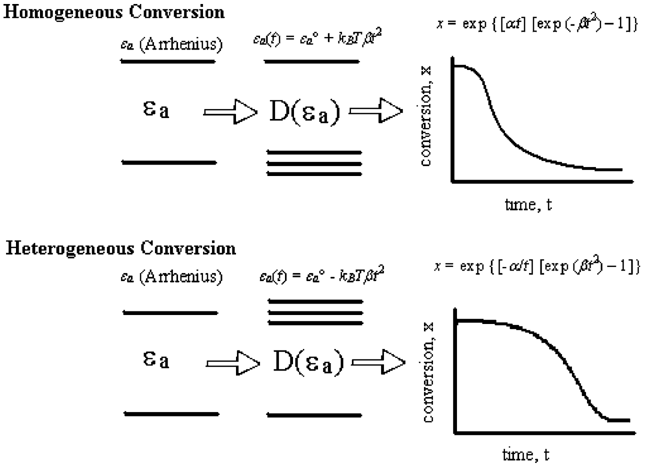

Figure 3. Schematic depiction of the key findings of this work, relating the differences between the dispersive kinetics of homogeneous (dimension = 2) and heterogeneous systems (dimension = 0); see text for details.

Supporting Information Available: A discussion of the empirical nature of traditional kinetic models and the semiempirical basis of the author's dispersive kinetic models is presented. Additionally, a discussion of a "three-dimensional Marcus theory" is presented to lend support to the idea of molecular motion serving as the basis for the majority of dispersive processes. This material is available free of charge via the Internet at http://pubs.acs.org.

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