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Statistical Thermodynamic Description of Homogeneous Dispersive Kinetics

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A statistical thermodynamic interpretation of homogeneous dispersive kinetics (which assumes the existence of a pseudo-equilibrium between a distribution of reagent states and a single activated state, which together define the rate-determining step), coupled with a previous "quantum kinetic" description for this same type of system (Skrdla, P. J. *J. Phys. Chem. A* 2006, *110*, 11494), is found to provide new insights into the kinetics of these conversions. In particular, the change in the (apparent) activation energy with conversion time is shown to be a function of the entropy change associated with the ensemble of reagent molecules as they traverse the activation energy barrier. Using these two "orthogonal" stochastic interpretations of dispersive kinetics, a fundamental physical description of the rate parameter β in the author's model is obtained.

Introduction

From the literature, it is known that the specific (i.e., concentration-independent) reaction rates of chemical reactions or physical transformations are strongly dependent on the efficiency of the over-barrier transitions (e.g., those that are thermally activated) or, in certain cases, quantum mechanical tunneling through the activation energy barrier. For conversions in which the activation energy is unique, the specific reaction rate (i.e., the rate constant) is single-valued. However, for systems exhibiting "dispersive kinetics", the activation energy evolves as the conversion proceeds, thus giving rise to a time-dependent rate constant. This change in the (apparent) activation energy, which is a function of the time/extent of conversion, is caused by a continuous "system renewal" (i.e., relaxation) as the conversion proceeds. Such renewals are often attributed to molecular motion occurring on a time scale that is similar to, or slower than, that of the actual conversion. The impact of this motion on the conversion rate gives rise to dispersive kinetics, examples of which include solid-state phase transformations, reactions of biomolecules, and electron transfer in viscous media.[1,2]

This article is one in a series of recent works in which a new approach for modeling/describing dispersive kinetics is developed. The author believes that many reactions and phase transformations involving the solid state (in particular, those that are rate-limited by nucleation/denucleation processes involving small "critical nuclei"; the rates of formation of these smaller nuclei lend themselves to a quantum mechanical description of the kinetics that might differ significantly from the kinetics predicted using classical nucleation theory) are inadequately described by traditional kinetic models that do not account for the quantized, molecular-level energy variations that might be responsible for causing the observed dispersion in the activation energy barrier and that utilize unitless (i.e., empirical) fit parameters. The author believes that the specific reaction rate of dispersive kinetic processes can be accurately described using a convolution of the Maxwell−Boltzmann (M−B) kinetic energy distribution and the traditional Arrhenius equation (which introduces the fixed, potential energy component of the overall activation energy barrier). The M−B distribution is used to describe the quantized energy differences that ultimately give rise to the activation energy distribution in dispersive conversions (e.g., assuming nucleation/denucleation of an ideal gas, as a first approximation). The Arrhenius equation is used to convert the activation energy distribution into a corresponding distribution of rate constants and, ultimately, a time-dependent expression for the overall, macroscopic (i.e., observable) rate constant of the conversion.[3,4]

For example, in many solid-state conversions, the M−B distribution can account for the differences in molecular reaction times that originate from variations in spatial location inside the condensed matter (i.e., it might take longer for a molecule residing within the condensed phase to react than one located at the surface). Note that these differences in reaction times can be related to corresponding differences in the (apparent) molecular activation energies via the Arrhenius equation, as mentioned above. Essentially, the author has attributed the origin of the dispersion to variations in the *kinetic energy* component of the overall activation energy, which are of similar magnitude to the (fixed) *potential energy* component, in commonly observed dispersive conversions.[4]

Focusing only on "homogeneous dispersive kinetics" for the purposes of this work (as opposed to "heterogeneous dispersive kinetics"[4]), the author's model (discussed more later), unlike other dispersive kinetic models in the literature, uses only two rate parameters (α and β) to fit isothermal conversion data. Both of the parameters have units in the time domain, thus allowing physical interpretation. In a previous work,[4] a physical interpretation for the rate parameter α was described. In the present work, the author provides a statistical thermodynamic treatment of his kinetic model that can be considered to parallel the work of Eyring (who considered only nondispersive, bimolecular reaction kinetics). The findings point toward a possible link between stochastic "activation entropy" evolution and the conversion time for dispersive kinetic processes. Using this approach, a physical interpretation for the rate parameter β is obtained.

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Results and Discussion

In classical kinetics (as described by the Arrhenius and Eyring equations), a unique activation energy barrier is typically defined between a set of reactants and products on a potential energy surface (PES) for elementary reactions or for each individual mechanistic step of a more complex conversion. For the latter processes, one is often most interested in the activation energy barrier of the rate-determining step (rds), as it has the highest value and thus it dictates the overall speed of the conversion. The author believes that, in systems exhibiting dispersive kinetics, the activation energy barrier (e.g., of the rds) should be defined stochastically, by utilizing the functional form of the M−B distribution.

Note that the author is generally not supportive of the traditional view of chemical kinetics in which only the fraction of molecules in the “high-energy tail” of the M−B distribution have sufficient energy to react. That is because this view is a static one and the study of kinetics inherently involves dynamic processes. Therefore, such an interpretation of “classical Arrhenius kinetics” is likely too simplistic to apply to dispersive processes.

As mentioned in the Introduction, if molecular dynamics is important in affecting the rate of reaction, dispersive kinetics is born. The author’s view of (homogeneous) dispersive kinetics is one in which the M−B distribution of molecular kinetic energies (and, consequently, activation energies) is allowed to morph over time, i.e., it is a function of the extent of conversion. Even at a constant temperature (as isothermal conditions are required for use of the author’s kinetic models), whereby this distribution can be expected to have a fixed shape, the continuous depletion (via reaction) of the molecules in the high-energy tail, and the subsequent attempt at redistribution of the remaining reagent molecules to re-form this tail, results in a varying fractional population of molecules that are available to react at any given time. (Note that this view of a microscopically “staged/segmented” reaction, with respect to time, is consistent with the idea of quantization of the activation energy barrier, which is inherent in the author’s use of the M−B distribution to define a distribution of molecular-level activation energies/rate constants.) Ultimately, the net result is a time-dependent rate constant/activation energy for the overall (macroscopic) conversion. Thus, it can be stated that homogeneous dispersive kinetics is governed by the limited ability of a given reagent population to redistribute thermal energy (i.e., to relax) on the time scale of the conversion. Conversely, classical Arrhenius kinetics (which can be adequately described by a single potential energy barrier of activation) applies to systems in which the thermalization is very rapid with respect to the reaction (and thus can be neglected in the treatment of the kinetics). Whereas the connection between temperature and (average molecular) kinetic energy is well-known, as is the effect of temperature on the reaction rate in systems exhibiting classical Arrhenius kinetics, the combined use of both kinetic and potential energies to describe the activation energy barrier in dispersive conversions is particular to the author’s works.

The author has defined two types of dispersive kinetics that are observable in the solid state: homogeneous and heterogeneous.[3−5] The former conversions have been characterized by dispersion in the kinetic energies of the *reagent species*, and they generally produce deceleratory, sigmoidal conversion versus time ($x-t$) profiles; examples of such conversions include certain (denucleation-rate-limited) solid-state thermal decompositions. On the other hand, heterogeneous dispersive processes are characterized by a similar variation in the kinetic energies pertaining to the *activated-state species*, and they generally produce acceleratory, sigmoidal $x-t$ profiles; examples include some (nucleation-rate-limited) crystallizations and polymorphic transformations. Note that, although both types of conversions generally produce asymmetric sigmoid transients, in heterogeneous/acceleratory processes, the inflection point occurs more toward the end of the conversion, whereas in homogeneous/deceleratory processes, the inflection point typically occurs earlier in the conversion. For the purposes of this work, only homogeneous dispersive kinetics is discussed, although the conclusions drawn are expected to hold similarly for heterogeneous systems (because they can be treated in a complementary manner[4]).

Using the Kohlrausch−Williams−Watts (KWW; stretched exponential) function and assuming molecular motion obeying the continuous-time random-walk (CTRW) model, the general form of the time-dependent rate constant in dispersive/“fractal time” kinetics can be defined as[1,2]

$$k = \Lambda^{\circ}(t/\tau)^{m-1} \exp(-\epsilon_a{}^{\circ}/k_B T) \tag{1}$$

where Λ° and $\epsilon_a{}^{\circ}$ represent the frequency factor and potential energy of activation, respectively (i.e., as per the Arrhenius equation); k_B is the Boltzmann constant; T is the absolute temperature; τ is the effective relaxation time; and m is an empirical dispersion parameter. From eq 1, the activation energy can be observed to vary with time according to the equation

$$\epsilon_a(t) = \epsilon_a{}^{\circ} + (1 - m)k_B T \ln(t/\tau) \tag{2}$$

For nucleation-rate-limited processes, the theory derived by Johnson and Mehl and Avrami, Erofe’ev, and Kolmogorov[1,2] has been applied widely in the literature since its development in the late 1930s/early 1940s. More recently, Plonka has shown that the so-called “JMAEK equation” is a general result of the above dispersive kinetics approach, which is based on the concept of fractal time.[6] The JMAEK equation can be written most simply as

$$x = \exp(-kt^n) \tag{3}$$

where x represents the fraction of reagent remaining in the system at time t. Unfortunately, the value of n in eq 3, which is unitless (and can be considered analogous to m), is often empirical because it does not precisely match any of the established mechanisms (i.e., those with $n = 2$, 3, or 4; for example, see ref 5) when fitting real kinetic data.

An alternative approach to modeling dispersive kinetics (that does not use fractals) was presented in the author’s previous works.[3−5] For isothermal, homogeneous dispersive processes, the author’s “semiempirical” dispersive kinetic model is given by[3,4]

$$x \approx \exp\{(\alpha t)[\exp(-\beta t^2) - 1]\} \tag{4}$$

where the (temperature-dependent) rate/fit parameters, α and β, have units of (time)$^{-1}$ and (time)$^{-2}$, respectively, and the variables x and t are defined as in eq 3. For such processes, the activation energy varies with the conversion time according to the expression[4]

$$\epsilon_a(t) \approx \epsilon_a{}^{\circ} + k_B T \beta t^2 \tag{5}$$

In Figure 1, two energy level diagrams, corresponding to two different homogeneous dispersive processes, are depicted schematically (side-by-side). Previously, a similar graphic was discussed in terms of both a kinetic energy distribution, $D(\epsilon)$,

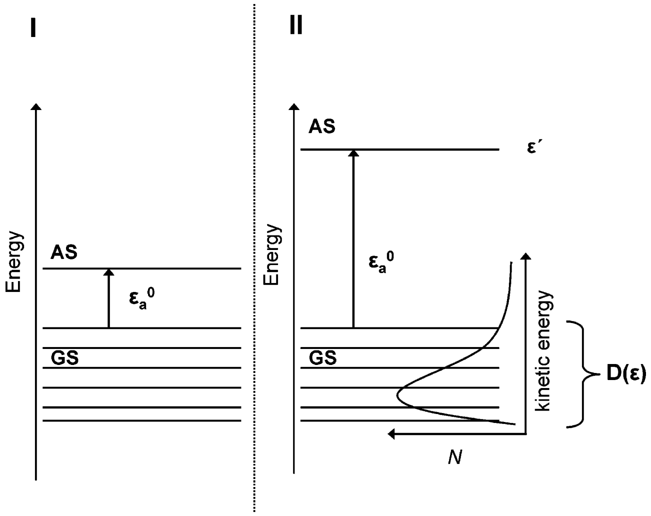

Figure 1. Schematic energy level diagram (not drawn to scale) for the rds of two homogeneous dispersive kinetic processes: System I has a lower activation energy potential, $\epsilon_a°$, whereas system II has a higher activation energy potential. The distribution of the reagent (GS) energy levels, $D(\epsilon)$, takes the functional form of the M−B kinetic energy distribution, as described in earlier works. $D(\epsilon)$ can also be described using statistical thermodynamics as discussed in the present work; in this case, the time-dependent activation energy, $\epsilon_a(t)$, increases as a function of the conversion time as a result of stochastic entropy loss accompanying the over-barrier transitions (see text for details). The energy of the activated state (AS) is considered to be single-valued in both cases. System I is more likely to exhibit characteristic dispersive kinetic behavior (i.e., to produce a deceleratory, sigmoidal $x-t$ profile) than system II.

and a fixed potential energy barrier, $\epsilon_a°$, to define $\epsilon_a(t)$.[4] However, the author believes that it should also be possible to define the dispersion (i.e., what is shown in the reagent/"monomer" population in the figure) in terms of thermodynamic quantities, by similarly utilizing a stochastic view of the kinetics. Such a description might be especially useful for understanding dispersive conversions in some processes (i.e., heterogeneous conversions) involving the solid state in which the key constituents are not readily mobile (i.e., it might not be easy to envision kinetic energy variations of molecules in condensed phases/critical nuclei) as they are in gas-phase reactions.

In the last century, Marcus theory showed that it is possible to predict activation energies in terms of classical thermodynamic quantities for simple unimolecular processes. Later, Eyring's transition state theory (TST) demonstrated, on the molecular level, the origin and physical behavior of the transition state (TS) species responsible for defining the activation energy barrier, this time, for simple bimolecular conversions. TST applies statistical mechanics to the rapid "pre-equilibrium" assumed to exist between the reagents and the TS species. Below, a similar attempt at applying statistical mechanics is described; however, this time it is used for the treatment of homogeneous dispersive conversions. The goal is to try to gain new insights into dispersive kinetics by linking both the thermodynamic and kinetic interpretations of these conversions. (Note, for example, that Mareš and Šesták implied a possible link between entropy and kinetic energy in a recent publication.[7])

For crystals, relatively low-energy quantized vibrations, called phonons, are responsible for solid-state properties such as thermal/electrical conductivity and sound travel. Thermal phonons can exhibit desirable properties for energy quantization in solids that can ultimately produce a distribution such as the one depicted schematically in Figure 1. Although phonons exhibit both particle-like and wave-like properties, they are generally classified as bosons with integer spin. In analogy with Planck's treatment of blackbody radiation, one can consider the phonons in a solid to be an ensemble of harmonic oscillators. Thus, Bose−Einstein (B−E) statistics can be used to describe the energy distribution of phonons in a given solid. However, B−E statistics is most useful at low temperatures/high concentrations (e.g., in a "B−E condensate") where the quantum concentration, n_q (i.e., the interparticle distance), is high; this occurs when $N/V \geq n_q$ (N is the number of molecules/atoms/ions occupying volume V). Furthermore, B−E statistics considers all of the particles in the ensemble to be indistinguishable. Although the M−B distribution effectively treats both B−E and Fermi−Dirac (F−D) statistics at high T, more importantly, it considers the particles in a crystal as being distinguishable. (As mentioned in the Introduction, because various monomers can occupy different spatial locations inside a given condensed phase, they can be expected to react at different times/with different activation energies.) For this reason, the author believes that the M−B (kinetic energy) distribution is superior to the other two energy distributions in describing general dispersive kinetic processes. Note also that, whereas Mareš and Šesták suggest the use of an electromagnetic description of the cohesive (van der Waals type) forces in condensed-matter quantum thermal physics,[7] the author believes that such a description is likely to be most valid for conductors (i.e., metals). For solid phases composed of drug molecules, for example, molecular forces including H-bonding, ionic, aliphatic, and $\pi-\pi$ interactions can also play a significant role in affecting the kinetic/thermodynamic properties of these systems. Thus, the author favors a general, stochastic kinetic model that does not make specific assumptions about the origins of the quantized energies.

Regardless of whether one chooses translational, rotational, or vibrational motion for the purposes of quantization in the present dispersive kinetic treatment, using statistical thermodynamics,[8,9] one can define the following general quantities for the monomer species in Figure 1

$$q = [1 - \exp(-\epsilon/k_BT)]^{-1} \tag{6}$$

$$U - U° = N\epsilon/[\exp(\epsilon/k_BT) - 1] \tag{7}$$

$$S = Nk_B\{(\epsilon/k_BT)/[\exp(\epsilon/k_BT) - 1] - \ln[1 - \exp(\epsilon/k_BT)]\} \tag{8}$$

where q is the partition function, ϵ represents the quantized energies, N is the number of monomers in the system, U is the total internal energy, $U°$ is the internal energy at $T = 0$ K, and S is the total entropy. Whereas eqs 6−8 pertain to the reagent-level (GS) distribution, as per the hypothetical homogeneous conversions depicted in Figure 1, for the activated state (AS), $q = 1$, $U - U° = N\epsilon'$, and $S = 0$. (Note that $U°$ is assumed to be the same for both the GS and the AS in the derivation below.) Assuming a pseudo-equilibrium between the GS and the AS (analogous to the assumption of Eyring) and using the change in the Helmholtz free energy (A_{act}) to define the activation energy, one finds that, for homogeneous dispersive processes

$$\begin{aligned} A_{act} = A_{AS} - A_{GS} = \Delta U_{act} - T\Delta S_{act} = \\ \{N\epsilon' - N\epsilon/[\exp(\epsilon/k_BT) - 1]\} + T(Nk_B\{(\epsilon/k_BT)/ \\ [\exp(\epsilon/k_BT) - 1] - \ln[1 - \exp(\epsilon/k_BT)]\}) \end{aligned} \tag{9}$$

From eqs 9 and 5, one can write two relations (by assuming that the solution is not unique)

$$E_a^\circ \approx N\{\epsilon' - \epsilon/[\exp(\epsilon/k_BT) - 1]\} \tag{10}$$

and

$$t \approx (\beta^{-1}N^{-1}k_B^{-1}\{(\epsilon/k_BT)/[\exp(\epsilon/k_BT) - 1] - \ln[1 - \exp(\epsilon/k_BT)]\})^{1/2} \tag{11}$$

Then, from eqs 8 and 11, it is trivial to obtain the result

$$\beta \approx \Delta S_{act}/Nk_Bt^2 = \Delta S_{act}/Rt^2 \tag{12}$$

where R is the gas constant. Thus, a relationship between the conversion time and the (stochastic) change in activation entropy has been obtained via the rate parameter β, which appears to serve as a link between the kinetic and thermodynamic descriptions of dispersive kinetics. In a slightly different form, eq 12 can be recast as

$$\Delta S_{act} \approx \pm R\beta t^2 \tag{13}$$

In eq 13, β can be seen to have a clear physical interpretation. (As mentioned earlier, the rate parameter α, which is also found in eq 4, was described in detail elsewhere.[4]) Also, as β is a constant, it can be either positive or negative depending on whether the conversion is heterogeneous/acceleratory or homogeneous/deceleratory, respectively;[4,5] for this reason the ± sign is shown explicitly in eq 13. Using eq 13 but omitting the ± sign, one can write the following results in terms of molar quantities [e.g., $E_a(t) = N\epsilon_a(t)$]

$$E_a(t) \approx E_a^\circ - T\Delta S_{act} \tag{14}$$

$$E_a^\circ \approx \Delta U_{act} \tag{15}$$

Equations 14 and 15 are thought to be general, i.e., applicable to all kinds of dispersive kinetics (e.g., those that can be modeled using eq 4 or its analogous equation for application to heterogeneous systems[4]). Note that, because the sign of β is negative for homogeneous dispersive conversions (it is responsible for producing deceleratory, sigmoidal $x-t$ profiles), in such systems, the activation energy generally increases with conversion time as a result of a loss in entropy resulting from the over-barrier transitions. The opposite is true for dispersive kinetics in heterogeneous systems, in which the sign of β is positive (and the sigmoidal $x-t$ trends are generally acceleratory in appearance).[3−5]

Conclusions

The combination of the author's previous quantum kinetic approach for treating dispersive kinetics with a new statistical thermodynamic treatment was able to provide new insights into dispersive kinetic processes. Specifically, it was found that the time dependence of the activation energy barrier (which is a common feature to all dispersive processes) for homogeneous dispersive conversions can be attributed to the stochastic change in entropy experienced by the ensemble of reagent molecules as they traverse the activation energy barrier. Ultimately, the treatment described in this work was successful in providing a physically relevant description of the rate parameter β that is used in the author's various dispersive kinetic models.

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