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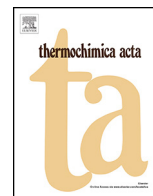


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ABSTRACT

Two dispersive kinetic models (DKMs) are used for the first time to precisely simulate the evolution of the activation energy barrier, ΔG^\ddagger , as a function of the extent of conversion, x , of hypothetical conversions with realistic physical parameters. The simulated ΔG^\ddagger - x plots closely resemble certain trends reported in the recent experimental literature obtained using so-called isoconversional methods of thermal analysis (TA), thus forging a new link between the experimental results and dispersive kinetics theory. The simulations provide unprecedented mechanistic insight into such data trends. It is easily deduced that the activation energy distributions underpinning the two DKMs are responsible for producing the distinct variations observed in ΔG^\ddagger . That is because DKMs utilize the concept of a distribution of activation energies to simultaneously treat the kinetics and dynamics that can be observed in elementary conversions and that classical kinetic models (CKMs), which assume a single activation energy to model just the kinetics in the absence of dynamical effects, cannot properly describe (Skrdla, 2013). While the use of DKMs in TA applications remains quite limited, the two DKMs considered herein have been discussed in detail elsewhere and their application to a host of different conversions/phase transformations has been demonstrated under isothermal conditions (Skrdla, 2009). In the present work, those DKMs are used to simulate non-isothermal ΔG^\ddagger - x trends. Through the course of these investigations, it is found that the simulated data sets also indicate that the heating (cooling) rate can have a dramatic impact on kinetic determinations, whereas current isoconversional methods, relying on classical kinetic theory, predict no such effect. The last finding points to a need to develop new thermal methods, based on the theory underpinning DKMs rather than CKMs, to more rigorously model dispersive kinetic processes that exhibit distributed reactivity.

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1. Introduction

1.1. Background and goals

So-called “complex conversions” in the thermal analysis (TA) literature are those processes whose kinetics are typically characterized by more than one activation energy barrier. Using isoconversional methods [1] to allow flexibility in the determination of the activation energy (ΔG^\ddagger) at each value of the extent of conversion (x), one can expect to observe non-linearity in plots of ΔG^\ddagger versus x produced by complex conversions. In the absence of multiple rate-limiting steps/competing reactions (that are mechanistically distinct from each other), it is also possible for a single, elementary conversion to exhibit complex kinetic behavior. In such

cases, it is the concurrent dynamical evolution—leading to system relaxation/continuous renewals [2]—occurring with a rate comparable to, or slower than, the rate of conversion that produces the variation in ΔG^\ddagger that can be observed experimentally.

An easy way to identify a dispersive kinetic process, which is underpinned by an activation energy distribution, $g(\Delta G^\ddagger)$, is by the sigmoidal (S-shaped, e.g. “Avrami-like”) nature of the conversion transient observed under isothermal conditions [3,4]. Such transients can be modeled in a deterministic manner using dispersive kinetic models (DKMs) [5].

Unfortunately, the majority of deterministic kinetic models found in the TA literature are classical kinetic models (CKMs) that do not consider dynamical effects. Indeed, CKMs inherently assume that the system relaxation is always much faster than the conversion rate and thus the dynamics have no bearing on the rate-limiting step (i.e. on the kinetics). Curiously, the reliance on CKMs appears to conflict with certain present-day understanding, e.g. of the fact that the spatial location of monomers inside of a crystal

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can affect their individual conversion rates [6]. Moreover, the use of CKMs is inconsistent with the notion of “distributed reactivity” [1] that is also a widely accepted idea in TA and, just as importantly, it is a foundational concept behind dispersive kinetic models (DKMs) [3]. As widespread usage of DKMs is currently lacking, in part because dispersive kinetics (including molecular and condensed phase dynamics) is an evolving field, one of the overarching goals of this work is simply to stimulate interest by demonstrating the potential utility of DKMs in TA.

The way in which different spatial location can affect the reactivity of a monomer inside a crystal lattice can be viewed in at least two different ways. Firstly, for a conversion that is initiated at the surface (e.g. at a grain boundary), one can expect that an interior monomer will convert later on during the process than a surface-bound one (and that the opposite should hold for a conversion beginning at a defect site inside of the crystal). The different conversion times necessarily correlate to different specific rates (a dynamic effect, rather than a kinetic one) and, consequently, to different activation energies (via the well-known Arrhenius equation). Alternatively, one can consider the different thermodynamic energies of the various spatially-distributed monomers (e.g. the number of nearest neighbors) [7] within the crystal as those energy variations can likewise affect the magnitude of the activation energy barrier facing each lattice monomer. In either case, the end result is a distribution of activation energies, $g(\Delta G^\ddagger)$, that must be considered in place of the single ΔG^\ddagger that is typically assumed with the use of CKMs via the assumption of a (single) rate constant [3]. Likewise, for processes that are nucleation or denucleation rate-limited and in which the system supersaturation is not fixed (by a continuous influx of monomers/crystals of the initial phase), the system relaxation dynamics naturally lead to the production of differently sized critical nuclei at different times during the conversion—thus, further contributing to the observation of mathematically smooth activation energy distributions [12].

In terms of deterministic models, only certain DKMs can properly describe processes in which there is inherent system heterogeneity, of the type discussed above, that gives rise to a multitude of specific rates/distribution of activation energies that is also known as “distributed reactivity” [1,5,8] in TA. In cases where the dynamics/system relaxation are sufficiently fast so as to allow them to be considered negligible in affecting the conversion rate, the DKM simply reduces to the CKM on which its derivation was based (the F1 model, in this work) due to the fact that $g(\Delta G^\ddagger)$ becomes infinitely narrow and, hence, a single-valued ΔG^\ddagger is recovered. Note that the terms “complex conversion”, “system relaxation”, “dynamical evolution”, “dispersive kinetics”, “distributed reactivity”, “system heterogeneity”, “non-linear ΔG^\ddagger - x plot”, “sigmoidal conversion transient”, “activation energy distribution”, “variable activation energy”, etc., can all be used interchangeably, as per this work, since they all relate the same fundamental behavior in the context of solid-state kinetics.

The advent of the isoconversional methods, beginning several decades ago, provided some of the earliest evidence of the existence of variable activation energy in solid-state kinetics [9]. In recent years, the concept has gained broader acceptance for two reasons: firstly, it has been widely reported to-date in experimental works and, secondly, there is sound rationale for such behavior, as per the above discussion. However, while isoconversional methods allow flexibility for the activation energy to evolve over the course of a given conversion, their derivation provides no clues as to why such behavior should be observed for certain conversions but not for others. In other words, they provide no mechanistic or physical insight to help rationalize the variability in ΔG^\ddagger . On the other hand, DKMs provide a concrete physicochemical basis for such variation, even for processes that are rate-limited by a single conversion mechanism (F1) over their entirety, as will be shown

in this work. Moreover, as each of the two DKMs presented herein is linked to a specific mechanism—either nucleation or denucleation (the complementary process to nucleation)—one can use the results of the simulations presented herein to potentially identify the rate-limiting process behind various literature data.

The two DKMs of interest here have been presented in the recent literature for application to isothermal data [4,5]—one describing so-called [1] “acceleratory” conversion transients and the other “decelerating” ones. In the present work, they are used in a brand new way to simulate the evolution of the activation energy, ΔG^\ddagger , as a function of the extent of conversion, x , at different heating rates (pertaining to non-isothermal conditions). The key goal of doing so is to determine whether the simulations can be used to explain with more physical rigor and mechanistic insight some of the distinctly curved ΔG^\ddagger - x plots reported previously in the experimental literature obtained using isoconversional methods [1]. Due to the prevalence of non-isothermal methods in the TA literature [1], the simulations are conducted at different heating rates, h , and the effect of such on the ΔG^\ddagger - x plots is also discussed.

1.2. Theory: dispersive kinetics

The derivation of most DKMs found in the literature can be traced to the following expression [8]:

$$x = \int_0^\infty \exp \left[- \int_0^t k \, dt \right] g(\Delta G^\ddagger) d\Delta G^\ddagger \quad (1)$$

From Eq. (1) it is clear that two factors are important in defining the DKM: the functional form of $g(\Delta G^\ddagger)$ and the time-dependence of k , the rate coefficient (not rate constant). Unfortunately, Eq. (1) does not explicitly require a physicochemical link between those two functionalities, unlike the author's (less direct) approach [5]. Naturally, the static description provided by $g(\Delta G^\ddagger)$ and the dynamical description of ΔG^\ddagger evolution as a function of time, t , should be directly mathematically relatable.

The derivation of the DKMs of interest here [5] begins with the use of the Maxwell–Boltzmann (M–B) distribution to relate not only the basic functional form of $g(\Delta G^\ddagger)$, but also to extract the approximately Gaussian t -dependence of k that was further probed in a recent work [10]. Unfortunately, as it is not possible to obtain analytic solutions to Eq. (1) using the M–B distribution directly (and/or the Gaussian functional form of k), the original derivation applied various simplifying approximations and assumptions discussed previously [5]. That was done to ensure that the DKMs do not require numerical methods for evaluation, thus allowing them to be readily used by experimentalists.

Acceleratory sigmoidal conversion transients [5,10,12] that are typically observed for nucleation-and-growth rate-limited processes [13–15] are often well-described by the DKM, below, that assumes a rate-limiting first-order (F1) conversion mechanism:

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

where x represents the fraction of product in the system at any time, t (i.e. the extent of conversion). The two fit parameters, α and β , have units of s and s^{-2} , respectively, and they have the following physical interpretations that are supported by classical kinetic theory in the t -independent limit (whereby, in cases when $\beta \rightarrow 0$ in Eq. (4), the second exponential term in square brackets never enters the derivation and thus Eq. (2) similarly reverts back to the classical F1 model):

$$\alpha = A^{n-1} e^{-\Delta H^\ddagger/RT} \quad (3)$$

$$\beta = \frac{\Delta S^\ddagger}{Rt^2} \quad (4)$$

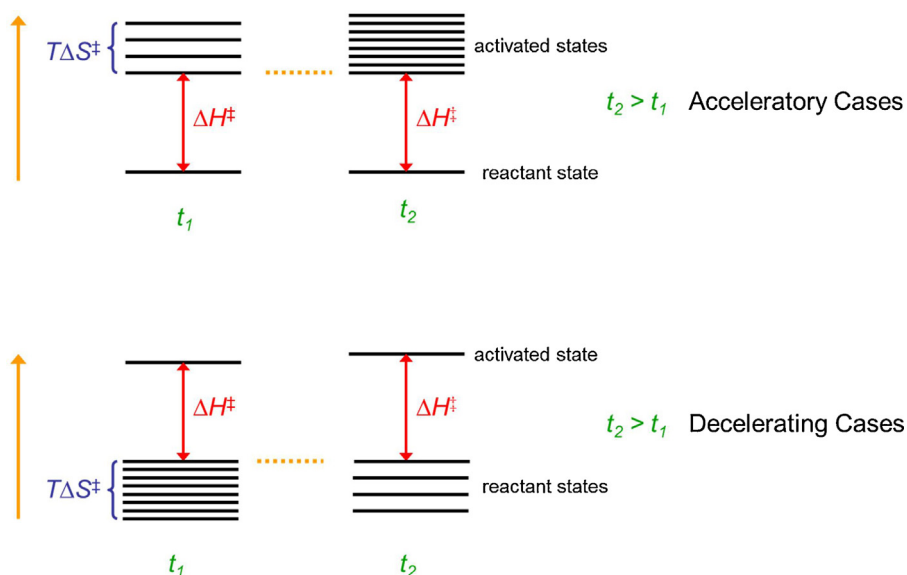


Fig. 1. Schematic illustration of the time-evolution of ΔG^\ddagger for acceleratory (top) and decelerating (bottom) type dispersive kinetic conversions. In acceleratory cases (e.g. nucleation-and-growth), the activation entropy increases as a function of t , while the opposite is true for decelerating/deceleratory-type (e.g. denucleation rate-limited) conversions.

where A is an Arrhenius-like frequency factor with the t -dependent entropic component explicitly removed from it (and whereby the t -independent component of ΔS^\ddagger remains part of the pre-exponential term in Eq. (3), suggesting that it can be evaluated using Eyring plots), ΔH^\ddagger is the activation enthalpy, ΔS^\ddagger is the t -dependent activation entropy, R is the gas constant and T is the absolute temperature. In Eq. (3), n is a constant that relates the dimensionality of the system; in the derivation of Eq. (2) it is assumed that $n=0$ as discussed elsewhere [5].

For acceleratory x - t sigmoidal transients, β is inherently positive while the opposite is true for decelerating conversions (examples of which include certain crystal decomposition and crystal dissolution processes that are denucleation rate-limited), discussed more below. Fig. 1 shows a schematic representation of the two different types of elementary dispersive kinetic processes, with regard to both the origin of $g(\Delta G^\ddagger)$ and the t -evolution of the overall ΔG^\ddagger experienced by the system over the course of the conversion. In acceleratory cases, the rate-limiting step involves the formation of critical nuclei that represent the activated state in the over-energy barrier process, as per the nucleation-and-growth mechanism [12]; for decelerating kinetics, the decomposition of such clusters into monomers is rate-limiting and it is the latter that are the activated state species. Consequently, in acceleratory processes there is an overall increase in ΔS^\ddagger as the conversion proceeds, effectively lowering ΔG^\ddagger as a function of t ; the opposite is true for decelerating kinetics whereby the rate slows down over the course of the conversion. For comparison, the specific rate (of elementary conversions) is assumed to be fixed in classical kinetic theory.

Fig. 2 depicts typical activation energy distribution shapes [11] for both acceleratory and decelerating conversions. Note that the activation energies are sampled in order from low to high values in decelerating conversions, while the opposite holds for acceleratory cases (that is due to the different sign that β takes in each case). In the classical limit of fast system relaxation, $|\beta| \rightarrow 0$, which in turn yields $k \approx \alpha$, i.e. as per a traditional rate constant.

Turning now to the case of decelerating, sigmoidal x - t transients, the following DKM (that is complementary to Eq. (2)) has proven useful [5]:

$$x = 1 - e^{\alpha t [e^{(-\beta t^2)} - 1]} \quad (5)$$

In Eq. (5), the rate parameters, α and β , are defined as before, however, α has units of inverse time (as per a traditional F1 rate constant) and β is explicitly shown to be negative to reflect the deceleration in the transient caused by the increase in ΔG^\ddagger over t (thus, curve-fits using that equation will return positive values). In the derivation [5] of the above DKM it was specified a priori that $n=2$ because denucleation is a surface-driven (two dimensional) process.

2. Results and discussion

Most kinetic determinations performed using TA apply a linear heating (cooling) gradient, i.e. non-isothermal conditions. It was recently discussed [3] that simply by using a rapid heating/cooling rate one can impart dynamical effects, i.e. distributed reactivity, to the conversion as a direct consequence of the finite thermalization rate of the sample. That effect was previously referred to

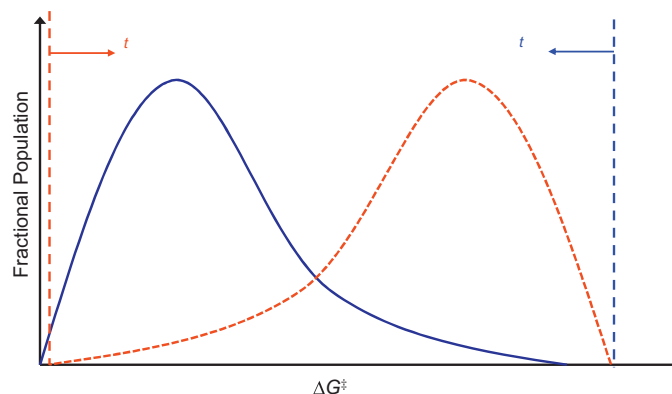


Fig. 2. Schematic depiction of the activation energy distribution (probability density) functions corresponding to the two DKMs discussed in this work: Eq. (2), for treating acceleratory sigmoidal x - t transients (blue, solid line curve), and Eq. (5), for relating decelerating trends (red, dashed line curve). As shown by the vertical broken lines, the two different activation energy distributions are sampled in opposite directions according to the sign of β —the blue curve is sampled starting from the highest activation energy at $t=0$, while the red distribution is sampled from low to high ΔG^\ddagger values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

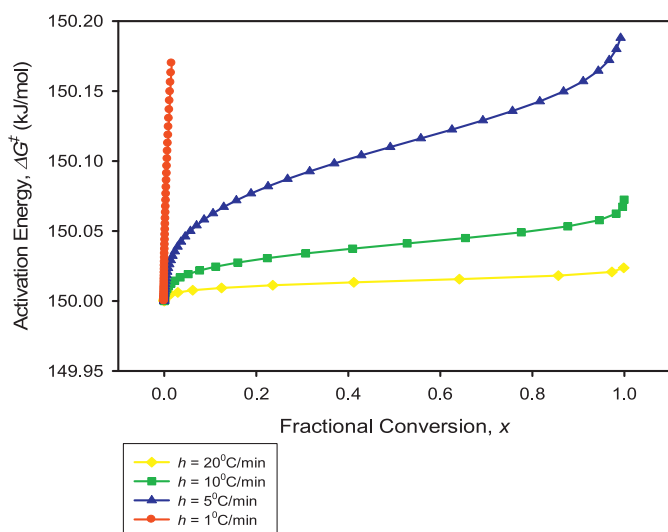


Fig. 3. Simulated curves of ΔG^\ddagger plotted as a function of x for a hypothetical, decelerating conversion ($n=2$, as per Eq. (5)) whereby: $\Delta H^\ddagger = 150 \text{ kJ/mol}$, $A = 10^{22} \text{ min}^{-1}$ and $\beta = -0.001 \text{ min}^{-2}$. Only every 10th data point is shown for clarity. The different heating rates, h , used to generate the plots are provided in the legend. The larger h values produce flatter profiles; see text for details.

as “dispersive kinetics of the second kind”, having the potential to affect both classical conversions described by CKMs and “first kind” dispersive kinetic conversions of the type described by the DKMs provided in Eqs. (2) and (5). Only first kind dispersive kinetic behavior is of interest in this work, which refers to conversions that exhibit dynamical effects even under isothermal conditions via the existence of an underlying activation energy distribution or, equivalently, a “manifold of transition states” [16] of the type discussed in the Section 1.

In Fig. 3 are shown simulated plots of ΔG^\ddagger – x at different linear heating rates, h , obtained using the DKM in Eq. (5). The simulated curves closely resemble plots reported in the recent experimental literature that were obtained using isoconversional methods (e.g. [8,17–24]), suggesting that the non-linearity in those plots not only reflects a class of conversions that exhibit distributed reactivity, but specifically pointing to a denucleation-type mechanism in the rate-limiting step.

It is noteworthy to point out that curve shapes of the kind shown in Fig. 3 have also been generated using simulations of single-step transformations with a fixed activation energy via the Flynn–Wall–Ozawa (FWO) method [25] that is known to provide a less accurate solution to the traditional temperature integral [1]. Alternatively, perturbations at both “low and high conversion degrees at the lower heating rates” can also be imparted to otherwise mostly flat ΔG^\ddagger – x profiles by introducing Gaussian-like random noise to data simulations, potentially suggesting that “these values must be interpreted with care” and leading some workers to consider applying a “simple smoothing algorithm” to the data [26]. Moreover, there is also the possibility of competing reactions [27] that is not considered herein due to the fact that the present work is concerned primarily with the kinetics and dynamics of single-step, elementary (specifically, F1) conversions. With regard to the first two points, however, in light of the results presented in Fig. 3 it would clearly be deleterious to immediately dismiss the observation of non-linearity as some artifact that is due, e.g. to the known higher degree of error in isoconversional methods that exists at the extremes. Likewise, the smoothing of experimental ΔG^\ddagger – x data or simply discarding the initial and final portions of a given data set is also not recommended because it can lead to a loss of dynamical information about the system (coming in via β) in the

case of dispersive kinetic conversions and, consequently, erroneous rate predictions. Of course, the system dynamics are reflected predominantly in the t -dependent ΔS^\ddagger term and are most pronounced at both low and high x values due to the inflection point at the center (also, in the limit $\beta \rightarrow 0$, the DKM would revert back to the F1 CKM with a completely flat ΔG^\ddagger – x profile).

It is furthermore clear from Fig. 3 that faster heating (cooling) rates serve to flatten out the observed ΔG^\ddagger – x profiles, potentially giving rise to what might appear to be a single value of the activation energy barrier at large $|h|$ values, mimicking the expected result for a classically behaved conversion with one rate-limiting mechanism operating over all x . This is a manifestation of a second kind (i.e. based in artifact) dispersive kinetic effect [3] whereby, for a first kind dispersive kinetic conversion of the type modeled by Eqs. (2) and (5), it is possible to sample $g(\Delta G^\ddagger)$ so quickly that it becomes impossible to accurately report on its true shape [11], as translated into the (empirically obtained or simulated) ΔG^\ddagger – x profile. Analogously, in chemical separations using chromatography it is commonplace to use, e.g. gradient elution rather than isocratic conditions to sharpen analyte peaks with the ultimate goal being to have infinitely narrow solute zones such that the resolution and peak capacity of the column are maximized. Of course, it is also understood in separation science that one must increase the sampling speed of the detector as the peaks become narrower in order to properly describe their shapes (and thus allow accurate analyte quantitation using the corresponding peak area).

It is important to note that the rather “unimpressive” variation in the activation depicted in Fig. 3 (excluding the $h = 1^\circ\text{C/min}$ plot), which falls within typical/expected experimental error of present-day isoconversional methods, is simply a function of the low β value arbitrarily selected for the simulations (as should become clear later; that is also why larger heating gradients were needed to show the activation energy variation). Because the simulation has no such error, it is possible to demonstrate the effect even on such a “weakly dispersive” conversion simply by magnifying the ordinate axis scale as per Fig. 3. Of course, larger β values have also been reported through curve-fitting of real-world kinetic transients obtained under isothermal conditions in the author’s previous referenced works, for example. The other kinetic parameters in the figure ($\Delta H^\ddagger = 150 \text{ kJ/mol}$, $A = 10^{22} \text{ min}^{-1}$) were selected (also arbitrarily) on the basis that they are of typical magnitude for a variety of conversions reported in the literature, including those in the author’s previous works.

In the simulations presented in Fig. 4, the dimensionality ($n=2$) was intentionally removed from Eq. (5) to show that the general shape of the ΔG^\ddagger – x plots is not dramatically affected by the magnitude of n . Additionally, the heating rates were substantially lowered relative to those shown in Fig. 3 to clarify the dependence of the plot curvatures on h . The effect of the degree of dispersion in the activation energy barrier, controllable via the magnitude of the β value [11], on the plots is also evident therein. Ultimately, one can see that smaller h values and/or larger $|\beta|$ values produce a higher degree of curvature, while the opposite is also true. While both findings are consistent with expectations, based on the underlying theory of DKMs briefly reviewed in the Introduction, no h -dependence of ΔG^\ddagger has been previously reported in the TA literature. As a point of interest, it is highlighted here that the former observation is simply an outcome of the t -dependence of ΔG^\ddagger that is well understood for first kind dispersive kinetic processes under isothermal conditions [2].

Fig. 5 shows simulated ΔG^\ddagger – x plots at different h and β values relevant to conversions that are nucleation-and-growth rate-limited—i.e. whose conversion transients can be precisely modeled using Eq. (2) under isothermal conditions [5]. While the same general behavior is observed as in the previous figures in that greater variation in the activation energy is triggered by

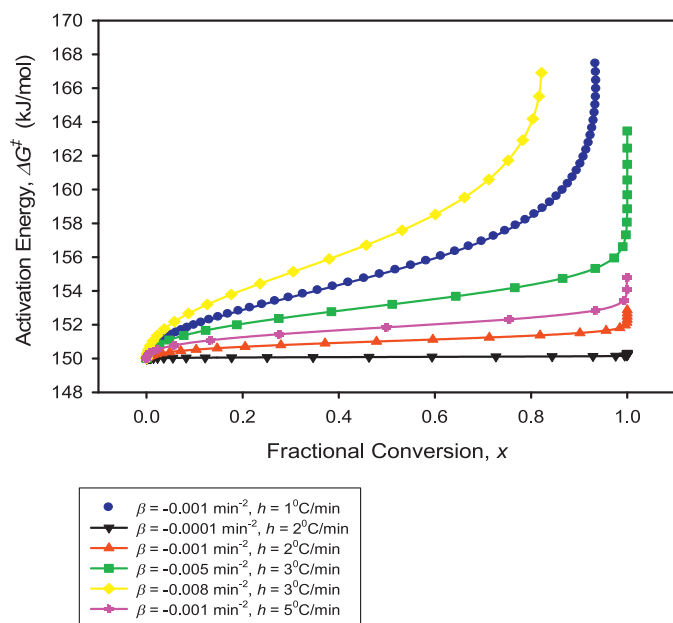


Fig. 4. Simulated curves of ΔG^\ddagger plotted as a function of x for a hypothetical, decelerating conversion (with $n=0$) that exhibits dispersive kinetic behavior, whereby: $\Delta H^\ddagger = 150$ kJ/mol and $A = 10^{22}$ min $^{-1}$. The different β and h values plotted are provided in the legend. Lower heating rates and larger $|\beta|$ values serve to exaggerate the curvature. The overall shape of the plots is not much impacted by the n value, as compared to Fig. 3.

lower heating rates and/or broader activation energy distributions, the curves in Fig. 5 resemble mirror images of those generated using Eq. (5). Empirical evidence for curve shapes of this kind can also be found in real-world data presented in previous literature [8,17,24,28–34], lending support to the importance of acceleratory dispersive kinetic conversions and, hence, the nucleation-and-growth mechanism in processes of interest to the TA community.

While the simulated ΔG^\ddagger - x curves provided by the DKMs presented in this work provide intriguing insights into many processes

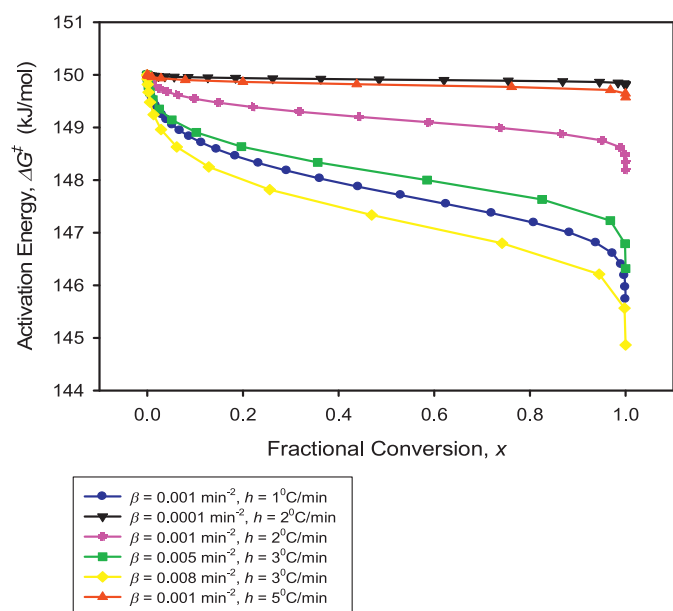


Fig. 5. Simulated curves of ΔG^\ddagger plotted as a function of x for a hypothetical, acceleratory ($n=0$) conversion modeled using Eq. (2), whereby: $\Delta H^\ddagger = 150$ kJ/mol and $A = 10^{22}$ min $^{-1}$. The various β and h values used are shown in the legend. The general shape of the plots is essentially opposite to those in Fig. 4.

reported in recent TA literature, there remains a lot more work to be done in modeling processes exhibiting distributed reactivity via isoconversional methods. In light of the t -dependence of the kinetic parameters (e.g. ΔG^\ddagger , k) in DKMs, which comes about as a direct consequence of the underlying distribution of activation energies, there is additional complexity that must be introduced to traditional thermal methods to allow them to more rigorously treat dispersive kinetics. For instance, the temperature integral that is solved numerically by most (integral) isoconversional methods is much simpler than the one that requires solving for use with DKMs, even under a fixed heating (cooling) rate [3]. And while it is commonplace these days to disregard ΔG^\ddagger values obtained at both low and high x values in performing isoconversional analyses, this work shows that valuable dynamical information about the conversion is potentially contained in those portions of the data. For the same reason, care should be taken to not use excessive heating (cooling) gradients that can artificially reduce the amount of variation observed in ΔG^\ddagger - x data of (first kind) dispersive kinetic processes.

3. Conclusions

Empirical ΔG^\ddagger - x data obtained using present-day isoconversional methods often show quite complex curvature that have proven quite challenging to interpret. The curves simulated in this work using two DKMs show that a substantial portion of those data might reflect (first kind) dispersive kinetic processes, thus allowing physicochemical/mechanistic rationalization of such data sets in an unprecedented manner. Moreover, the simulations suggest that more accurate rate predictions might be achievable via the use of DKMs and/or thermal methods modified appropriately to capture the key traits of dispersive kinetic conversions. That is because the curvature in each ΔG^\ddagger - x plot is simply a manifestation of the activation energy distribution underpinning each DKM [5,11,12] that describes the dynamical evolution of the system that occurs concurrently with the conversion. More accurate kinetic characterization of systems exhibiting distributed reactivity can be achieved by utilizing most of the ΔG^\ddagger - x profile rather than a small subset of it.

This work represents a first step toward demonstrating a fundamental understanding of non-linear ΔG^\ddagger - x data sets whereby the activation energy variability is not simply an artifact of the measurement and/or of the thermal method. While isoconversional methods have identified such variation in real-world data sets over recent decades, they have done so simply by not constraining the activation energy, i.e. by virtue of being largely “model (CKM)-free” [1]. Moreover, isoconversional methods have known errors that can cloud the interpretation of empirical data. On the other hand, DKMs predict a priori variation in ΔG^\ddagger - x data sets that comes as a natural consequence of the distributed reactivity associated with certain conversion mechanisms, without experimental error. Also, DKMs can tell us, e.g. why there is variability in the activation energy in some systems, but not in others, while simultaneously allowing one to extract physical parameters to quantify the underlying dynamical effects in cases where they are observed—whether it is via modeling or by simulation. Together with its preceding work [3], this paper points out certain limitations of current thermo-analytical methods, kinetic models and experimental practices as well as highlighting a strategy for performing more rigorous kinetic determinations of systems that do not behave classically.

References

- [1] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, ICTAC kinetics committee recommendations for performing

- kinetic computations on thermal analysis data, *Thermochim. Acta* 520 (2011) 1–19.
- [2] A. Plonka, Dispersive kinetics, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* 97 (2001) 91–147.
 - [3] P.J. Skrdla, Dynamical considerations for kinetic methods in thermal analysis, *J. Phys. Chem. Solids* 74 (2013) 1375–1379.
 - [4] Note that under an applied (fixed) heating/cooling rate, even a simple F1 exponential conversion transient takes on a sigmoidal shape, e.g. see: A. Khawam, D.R. Flanagan, Basics and applications of solid-state kinetics: a pharmaceutical perspective, *J. Pharm. Sci.* 95 (2006) 472–498, thus, it is easiest to determine if a conversion is dispersive (and whether it is acceleratory or decelerating) or classically behaved by examining the isothermal transient.
 - [5] P.J. Skrdla, Crystallizations, solid-state phase transformations and dissolution behavior explained by dispersive kinetic models based on a Maxwell–Boltzmann distribution of activation energies: theory, applications and practical limitations, *J. Phys. Chem. A* 113 (2009) 9329–9336.
 - [6] S. Vyazovkin, On the phenomenon of variable activation energy for condensed phase reactions, *New J. Chem.* 24 (2000) 913–917.
 - [7] P.J. Skrdla, Atomistic description of two-dimensional hexagonal close packed critical nuclei exhibiting quantization of the activation energy barrier, *Cryst. Growth Des.* 13 (2013) 1970–1977.
 - [8] A.K. Burnham, R.L. Braun, Global kinetic analysis of complex materials, *Energy Fuels* 13 (1999) 1–22.
 - [9] S. Vyazovkin, Kinetic concepts of thermally stimulated reactions in solids: a view from a historical perspective, *Int. Rev. Phys. Chem.* 19 (2000) 45–60.
 - [10] P.J. Skrdla, Investigation into the Gaussian time-dependence of the rate coefficient in dispersive kinetic models applied to simple gas-phase chemical reactions, *Mol. Phys.* 112 (2014) 97–100.
 - [11] P.J. Skrdla, Activation energy distributions predicted by dispersive kinetic models for nucleation and denucleation: anomalous diffusion resulting from quantization, *J. Phys. Chem. A* 115 (2011) 6413–6425.
 - [12] (a) P.J. Skrdla, Use of dispersive kinetic models for nucleation and denucleation to predict steady-state nanoparticle size distributions and the role of Ostwald ripening, *J. Phys. Chem. C* 116 (2012) 214–225;
(b) P.J. Skrdla, Correction to: use of dispersive kinetic models for nucleation and denucleation to predict steady-state nanoparticle size distributions and the role of Ostwald ripening, *J. Phys. Chem. C* 117 (2013) 13337–13338.
 - [13] P.J. Skrdla, R.T. Robertson, Semi-empirical equations for modeling solid-state kinetics based on a Maxwell–Boltzmann distribution of activation energies: applications to a polymorphic transformation under crystallization slurry conditions and to the thermal decomposition of AgMnO_4 crystals, *J. Phys. Chem. B* 109 (2005) 10611–10619.
 - [14] P.J. Skrdla, Roles of nucleation, denucleation, coarsening and aggregation kinetics in nanoparticle preparations and neurological disease, *Langmuir* 28 (2012) 4842–4857.
 - [15] P.J. Skrdla, Physicochemically relevant modeling of nucleation-and-growth kinetics: investigation of additive effects on the solvent-mediated phase transformation of carbamazepine, *Cryst. Growth Des.* 8 (2008) 4185–4189.
 - [16] J. Anwar, D. Zahn, Uncovering molecular processes in crystal nucleation and growth by using molecular simulation, *Angew. Chem. Int. Ed.* 50 (2011) 1996–2013.
 - [17] S. Vyazovkin, N. Sbirrazzuoli, Isoconversional kinetic analysis of thermally stimulated processes in polymers, *Macromol. Rapid Commun.* 27 (2006) 1515–1532.
 - [18] S. Vyazovkin, I. Dranca, X. Fan, R. Advincula, Degradation and relaxation kinetics of polystyrene–clay nanocomposite prepared by surface initiated polymerization, *J. Phys. Chem. B* 108 (2004) 11672–11679.
 - [19] J.D. Peterson, S. Vyazovkin, C.A. Wight, Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene), *Macromol. Chem. Phys.* 202 (2001) 775–784.
 - [20] D.S. Achilias, M.M. Karabela, I.D. Sideridou, Thermal degradation of light-cured dimethacrylate resins. Part I. Isoconversional kinetic analysis, *Thermochim. Acta* 472 (2008) 74–83.
 - [21] A.E. Jablonski, A.J. Lang, S. Vyazovkin, Isoconversional kinetics of degradation of polyvinylpyrrolidone used as a matrix for ammonium nitrate stabilization, *Thermochim. Acta* 474 (2008) 78–80.
 - [22] G.Z. Papageorgiou, D.S. Achilias, G.P. Karayannidis, Estimation of thermal transitions in poly(ethylene naphthalate): experiments and modeling using isoconversional methods, *Polymer* 51 (2010) 2565–2575.
 - [23] M.F. Kotkata, Sh.A. Mansour, Crystallization process analysis for $\text{Se}_{0.95}\text{In}_{0.05}$ and $\text{Se}_{0.90}\text{In}_{0.10}$ chalcogenide glasses using the contemporary isoconversional models, *J. Therm. Anal. Calorim.* 103 (2011) 957–965.
 - [24] M. Popović, J. Budinski-Simendić, M. Jovičić, J. Mursics, Diporović-Momčilović, J. Pavličević, I. Ristić, Curing kinetics of two commercial urea–formaldehyde adhesives studied by isoconversional method, *Hem. Ind.* 65 (2011) 717–726.
 - [25] J. Farjas, P. Roura, Isoconversional analysis of solid state transformations, *J. Therm. Anal. Calorim.* 105 (2011) 757–766.
 - [26] N. Sbirrazzuoli, L. Vincent, A. Mija, N. Guigo, Integral, differential and advanced isoconversional methods: complex mechanisms and isothermal predicted conversion–time curves, *Chemom. Intell. Lab. Syst.* 96 (2009) 219–226.
 - [27] J.M. Criado, P.E. Sánchez-Jiménez, L.A. Pérez-Maqueda, Critical study of the isoconversional methods of kinetic analysis, *J. Therm. Anal. Cal.* 92 (2008) 199–203.
 - [28] N. Sbirrazzuoli, S. Vyazovkin, A. Mititelu, C. Sladic, L. Vincent, A study of epoxy-amine cure kinetics by combining isoconversional analysis with temperature modulated DSC and dynamic rheometry, *Macromol. Chem. Phys.* 204 (2003) 1815–1821.
 - [29] S. Vyazovkin, N. Sbirrazzuoli, I. Dranca, Variation of the effective activation energy throughout the glass transition, *Macromol. Rapid Commun.* 25 (2004) 1708–1713.
 - [30] K.N. Lad, R.T. Savalia, A. Pratap, G.K. Dey, S. Danerjee, Isokinetic and isoconversional study of crystallization kinetics of a Zr-based metallic glass, *Thermochim. Acta* 473 (2008) 74–80.
 - [31] A.A. Abu-Sehly, Variation of the activation energy of crystallization in $\text{Se}_{81.5}\text{Te}_{16}\text{Sb}_{2.5}$ chalcogenide glass: isoconversional analysis, *Thermochim. Acta* 485 (2009) 14–19.
 - [32] A.S. Soltan, A study of DSC non-isothermal pre-crystallization kinetics of $\text{Pb}_{10}\text{Se}_{90}$ glass using isoconversional kinetic analysis, *Physica B* 405 (2010) 965–968.
 - [33] M. Abu El-Oyoun, DSC studies on the transformation kinetics of two separated crystallization peaks of $\text{Si}_{12.5}\text{Te}_{87.5}$ chalcogenide glass: an application of the theoretical method developed and isoconversional method, *Mater. Chem. Phys.* 131 (2011) 495–506.
 - [34] P.J. Skrdla, R.T. Robertson, Dispersive kinetic models for isothermal solid-state conversions and their application to the thermal decomposition of oxacillin, *Thermochim. Acta* 453 (2007) 14–20.