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Dispersive kinetic models predict variation of the activation energy with extent of conversion observed experimentally in isoconversional data

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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, $\Delta G^{\ddagger}$, as a function of the extent of conversion, x, of hypothetical conversions with realistic physical parameters. The simulated $\Delta G^{\ddagger}$–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 $\Delta G^{\ddagger}$. 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 $\Delta G^{\ddagger}$–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.

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 ($\Delta G^{\ddagger}$) at each value of the extent of conversion (x), one can expect to observe non-linearity in plots of $\Delta G^{\ddagger}$ 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 $\Delta G^{\ddagger}$ 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 $\Delta G^\ddagger$ 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 $\Delta G^\ddagger$ is recovered. Note that the terms “complex conversion”, “system relaxation”, “dynamical evolution”, “dispersive kinetics”, “distributed reactivity”, “system heterogeneity”, “non-linear $\Delta G^\ddagger$–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 $\Delta G^\ddagger$. 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, $\Delta G^\ddagger$, 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 $\Delta G^\ddagger$–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 $\Delta G^\ddagger$–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]:

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

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 $\Delta G^\ddagger$ 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:

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

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 $\beta \to 0$ 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):

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

$$\beta = \frac{\Delta S^\ddagger}{Rt^2} \tag{4}$$