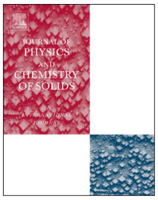
Journal of Physics and Chemistry of Solids 74 (2013) 1375–1379

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Dynamical Considerations for Kinetic Methods in Thermal Analysis

Peter J. Skrdla*

640 Maple Street, Westfield, NJ 07090, USA

ARTICLE INFO

Article history:
Received 21 June 2012
Received in revised form
16 April 2013
Accepted 25 April 2013
Available online 6 May 2013

Keywords:
C. Thermogravimetric analysis (TGA)
C. Differential scanning calorimetry (DSC)
D. Thermodynamic properties
D. Phase transitions

ABSTRACT

Popular kinetic methods of thermal analysis (TA) typically do not properly account for system dynamics (relaxation processes) that give rise to distributed reactivity, referred to here as “dispersive kinetics of the first kind”. In this work, new thermoanalytical relationships are put forth that allow more rigorous treatment of dispersive kinetics via the well-known Avrami-Erofe’ev (A–E) model, as it applies to both isothermal and non-isothermal (fixed heating/cooling rate) conditions. Simulated data is provided to highlight the errors that can arise from combining classical (non-dispersive, Arrhenius-based) kinetic treatments with the (dispersive) A–E mechanism. Lastly, “dispersive kinetics of the second kind” is discussed in the context of heating (cooling) a sample faster than it can thermalize. As shown by simulated data, doing so can impart dynamical effects even to conversions that would otherwise exhibit classical Arrhenius behavior.

1. Introduction

Thermal analysis (TA)[1] allows determination of solid-state kinetics using either isothermal or non-isothermal methods that, in turn, can be model-based or model-free[2]. While various thermal methods have been developed over recent decades, with both new model-based[3] and model-free[4] (so-called “isoconversional”) methods continuing to be put forth, the substantial variability/complexity often associated with the results does not lend much confidence to the use of TA methods for performing rigorous kinetic characterizations (or accurate rate predictions based on them). That is especially true in light of the controversy e.g.[5,6] that recently gripped the field, ultimately sparking a significant undertaking designed to standardize both experimental approaches and data treatments to try to reduce errors and ensure the reproducibility of results[7–11]. Of interest here, it has been stated that “kinetic parameters obtained by both isothermal and non-isothermal experiments usually are not in agreement“ [12], with examples of such being reported to the present time [13].

This work interrogates the basic hypothesis that it is the system dynamics (relaxation effects) exhibited by many solid-state conversions that complicates their kinetic characterization, due to the fact that such behavior is beyond the reach of popular thermal methods. Such dynamical effects, which are often manifested as “distributed reactivity” [14,15], require the use of dispersive kinetic models (DKMs) in place of the classical kinetic models (CKMs) typically found in the literature [2]. While all DKMs are underpinned by the concept of a distribution of activation energies [16], it is noteworthy that for cases where the system relaxation is fast relative to the conversion rate, the DKMs revert back to the CKMs on which their derivation is based. That is because the condition of fast relaxation allows the distribution to collapse to the classical limit of a unique activation energy barrier (and the corresponding Arrhenius rate constant, shown below). Thus, CKMs can be considered to represent a special case of their more general, DKM counterparts.

2. Theory behind traditional TA methods

2.1. Isothermal kinetics

Neglecting pressure (*P*) effects [1][1] on the kinetics, the rate is often parameterized in terms of the extent of conversion, α, and the temperature, *T*, starting with the equation [2]:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where $f(\alpha)$ is the differential form of the solid-state kinetic model [2] applicable to the system under investigation and *k* is the rate constant of the conversion. The Arrhenius equation is traditionally used to relate the *T*-dependence of *k*

$$k = A\exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

where *A* is the Arrhenius constant[2], E_a is the activation energy and *R* is the universal gas constant. Together, Eqs. (1) and (2) yield the

---

* Tel.: +1 908 361 1548.
E-mail address: skrdla@verizon.net

[1] This is a major assumption for gas-evolving/consuming reactions, particularly those in confined environments.

[2] The frequency factor in the Eyring equation is *T*-dependent, so assuming *A* is not *T*-dependent might be an important consideration for future error analyses.

0022-3697/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jpcs.2013.04.016

following result that “provides a basis for differential kinetic methods” [2]:

$$\frac{d\alpha}{dt}=A\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{3}$$

The analogous form to Eq. (3), for use in integral kinetic methods, is written as follows [2]:

$$g(\alpha)\equiv\int_0^\alpha\frac{d\alpha}{f(\alpha)}=A\int_0^t e^{\frac{-E_a}{RT}}dt \tag{4}$$

where the term, $g(\alpha)$, defines the integral form of the conversion model (that corresponds to $f(\alpha)$ in Eq. (3)). From Eq. 4 it is clear that the familiar equality, $g(\alpha)=kt$, applies only to cases where isothermal conditions are maintained and where k (or, likewise, E_a) is independent of t, thus allowing the above integral to be solved analytically.

Expressing Eq. (1) in logarithmic form and then taking its differential with respect to T^{-1} yields the equation, below, at a fixed value of α:

$$\left[\frac{\partial\ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha=\left[\frac{\partial\ln(k)}{\partial T^{-1}}\right]_\alpha+\left[\frac{\partial\ln(f(\alpha))}{\partial T^{-1}}\right]_\alpha \tag{5}$$

Eq. 5 illustrates the so-called “isoconverisonal principle” that states that the reaction rate at a constant extent of conversion is only a function of temperature. Since at any given α, $f(\alpha)$ is also a constant, the second term on the right hand side of the equation effectively disappears. Introducing Eq. (2) into Eq. (5), one can derive the relationship, below, from which it is easy to see why many isoconversional methods are often called “model free“[2]:

$$\left[\frac{\partial\ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha=-\left[\frac{E_a}{R}\right]_\alpha \tag{6}$$

2.2. Non-isothermal kinetics

Given the prevalence of non-isothermal methods in the current TA literature, it is of interest here that Eqs. ce:cross-refs id="crs0040" refid="eq0015 eq0020">3 and 4 can also be used to derive the following equations for application to non-isothermal kinetics [2]:

$$\beta\frac{d\alpha}{dT}=A\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{7}$$

$$g(\alpha)=\frac{A}{\beta}\int_{T_0}^T e^{\frac{-E_a}{RT}}dT \tag{8}$$

Both Eqs. (7) and (8) use the standard definition of the heating (cooling) rate given by the relationship, $\beta=dT/dt$, whereby $\beta=(T-T_0)/(t-t_0)=$constant for a fixed/linear gradient.

Eqs. (7) and (8) lay the foundation [2] of the differential, isoconversional Friedman method [19] and the integral, isoconversional methods of Dolye [20], Ozawa [21] and/or Flynn and Wall [22], Kissinger/Akahira/Sunose [23], Vyazovkin [24] and, more recently, Li and Tang [25], Cai and Chen [26], Roduit [27], as well as Farjas and Roura [4]. The latter methods numerically solve the so-called “temperature integral”, shown in Eq. 8, with evermore precise/rapid approaches. Eq. 7 and Eq. 8 also gave birth to the non-isothermal method of Kissinger [28] (that allows fitting kinetic data to a reaction model) and the non-isothermal, model-fitting methods of Freeman and Carroll [29,30] as well as Coats and Redfern [31,32].

3. Results and discussion

3.1. Dispersive kinetics of the first kind

The inherent heterogeneity of condensed phased matter can impart variation to the activation energy of conversions that can manifest itself in kinetic data, via dynamical/relaxation effects, in the form of sigmoidal (*S*-shaped) conversion transients observed under isothermal conditions [33]. An example of that kind of heterogeneity is the different spatial locations/environments of monomers in a given crystal lattice (e.g., interfacial versus interior/bulk sites). In cases where the rate-limiting step of the conversion involves the formation/dissociation of nuclei, those energy differences can become increasingly important because as the particles become smaller, the relative energy differences among the monomers get larger. Such variation can lead to distributed reactivity that necessitates treatment via dispersive kinetic theory/DKMs [14], as opposed to classical Arrhenius kinetics/CKMs.

Examples of processes that exhibit inherent dispersive kinetic behavior include nucleation and denucleation rate-limited conversions, for which relevant relationships have been presented in detail elsewhere [14]. Those conversions exhibit a dynamical evolution of k with t under isothermal conditions that stems directly from the underlying distribution of activation energies [16]. Traditional thermal methods based on Eq. (2), which depicts a unique rate constant, are clearly ill-equipped to handle such systems [15].

For illustrative purposes, the Avrami-Erofe’ev (A–E) model is considered in this work because it is widely used in the TA literature [2], yet it has also been discussed, separately, to be a DKM [16]. The A–E model has a general form, of dimensionality n, that can be written as

$$f(\alpha)=n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}\quad;\quad g(\alpha)=[-\ln(1-\alpha)]^{1/n} \tag{9}$$

The dispersive kinetic nature of the model can be seen from the rate coefficient (not constant), k, which has the following t-dependence [34]:

$$k=k_0t^{n-1}\ ,\ 0<n\le 1 \tag{10}$$

where k_0 is the classical rate constant (corresponding to $E_a{}^0$, as per Eq. (2)) for the conversion in the absence of the inherent dynamical effects. Indeed, if $n=1$, i.e., provided that the system relaxation dynamics are much faster than the specific conversion rate (of the rate-limiting step of interest), then the A–E mechanism reduces to the “F1” CKM [2].

Eq. (10) gives rise to the following relationship [34] for the evolution of E_a as a function of t:

$$E_a=E_a^0+(1-n)RT\ln(k_0t) \tag{11}$$

that has been reported elsewhere [16,34].

For dispersive kinetic conversions obeying the A–E mechanism, under a fixed heating (cooling) rate, the non-isothermal Eq. (7) gives rise to the following relationship

$$\beta^n\frac{d\alpha}{dT}=\left\{\left[A\exp\left(\frac{-E_a^0}{RT}\right)\right](T-T_0)^{n-1}\right\}\left\{n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}\right\} \tag{12}$$

Similarly, under equivalent conditions, Eq. (8) yields:

$$[-\ln(1-\alpha)]^{1/n}=\frac{A}{\beta^n}\int_{T_0}^T e^{\frac{-E_a^0}{RT}}(T-T_0)^{n-1}dT \tag{13}$$

While Eqs. (12) and (13) differ from the relationships normally found in the TA literature, they are thought to more accurately reflect the A-E mechanism in that they properly account for the t (T)-dependence of k presented in Eq. (10). Note also that the