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Thermochimica Acta 453 (2007) 14–20

thermochimica acta

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Dispersive kinetic models for isothermal solid-state conversions and their application to the thermal decomposition of oxacillin

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Received 16 October 2006; received in revised form 2 November 2006; accepted 6 November 2006
Available online 16 November 2006

Abstract

The authors recently published works in which the use of two novel equations for modeling the dispersive kinetics observed in various solid-state conversions are described. These equations are based on the assumptions of a 'Maxwell–Boltzmann (M–B)-like' distribution of activation energies and a first-order rate law. In the present work, it is shown that it may be possible to expand the approach to include mechanisms other than first-order, i.e. some of those commonly encountered in the field of thermal analysis, thus obtaining 'dispersive versions' of these kinetic models. The application of these dispersive kinetic models to the slightly sigmoidal, isothermal conversion–time (*x*–*t*) data of Rodante and co-workers for the degradation of the antibiotic, oxacillin, is described. This is done in an effort to test the limitations of the proposed dispersive models in describing kinetic data which is not clearly sigmoidal (i.e. as shown in previous works). Finally, it is demonstrated that, using graphical analysis, the typically sigmoidal *x*–*t* plots of first-order dispersive processes are the direct result of (asymmetric) activation energy distributions that are either '∩-shaped' (for heterogeneous conversions) or '∪-shaped' (for homogeneous conversions) in appearance, i.e. when the activation energy is plotted as a function of conversion. This finding lends support to the founding hypothesis of the authors' approach for modeling dispersive kinetic processes: the existence of 'M–B-like' distributions of activation energies.

Keywords: Oxacillin; Dispersive kinetic model; Activation energy distribution; Thermal decomposition

1. Introduction

While several common kinetic models exist in the literature for solid-state applications [1–4], their general application is often limited only to certain, simple phase transformations. These models are summarized in the first few columns of Table 1. For more complex transformations, generally those which exhibit multiple activation energies over the course of the conversion (as observed using 'model-free' isoconversional kinetic techniques [5–7]), these kinetic models, used either individually or in combination, often fail to adequately describe the data; a specific example will be discussed later in this work. Additionally, the traditional kinetic models are often plagued by factors including poor fits to experimental data, the inability to accurately estimate the start time of conversion, the empirical nature of the (sometimes many) fit parameters, etc. Alternatively, the authors have recently discussed the development of two novel, simple, 'dispersive kinetic models' which were shown to fit/describe well the experimental data for various solid-state conversions, including a solvent-mediated polymorphic transformation and a thermal decomposition, using only two fit parameters (each of which has physical units) [8].

Dispersive kinetics are observed in chemical systems exhibiting 'renewing environments', i.e. typically those in which molecular dynamics impact the measured rate of conversion [10–12]. The authors believe that many solid-state conversions may fall into this category (e.g. nucleation/de-nucleation and nucleation-and-growth, rate-limited processes, in which kinetic energy quantization may be important in affecting the conversion rate e.g. [9]). Dispersive kinetics are often explained by the existence of a distribution of activation energies. This distribution of activation energies, in turn, relates a time-dependent rate constant for the conversion, which can impact the observed kinetic behavior [8–12].

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doi:10.1016/j.tca.2006.11.004

Table 1
Compilation of common kinetic models used in condensed phase kinetics and novel dispersive variants for similar applications

Classical model	Differential form, $f(x)$	Integral form, $g(x)$	Dispersive model using $-\beta$, $n=2$	Dispersive model using $+\beta$, $n=0$
Avrami–Erofe'ev (A2)	$2(1-x)[-\ln(1-x)]^{1/2}$	$[-\ln(1-x)]^{1/2}$	n/a	n/a
Avrami–Erofe'ev (A3)	$3(1-x)[-\ln(1-x)]^{2/3}$	$[-\ln(1-x)]^{1/3}$	n/a	n/a
Avrami–Erofe'ev (A4)	$4(1-x)[-\ln(1-x)]^{3/4}$	$[-\ln(1-x)]^{1/4}$	n/a	n/a
Power Law (P2)	$2x^{1/2}$	$x^{1/2}$	n/a	n/a
Power Law (P3)	$3x^{2/3}$	$x^{1/3}$	n/a	n/a
Power Law (P4)	$4x^{3/4}$	$x^{1/4}$	n/a	n/a
Contracting area (R2)	$2(1-x)^{1/2}$	$1-(1-x)^{1/2}$	n/a	n/a
Contracting volume (R3)	$3(1-x)^{2/3}$	$1-(1-x)^{1/3}$	n/a	n/a
1D diffusion (D1)	$1/2x$	x^2	n/a	n/a
2D diffusion (D2)	$[-\ln(1-x)]^{-1}$	$(1-x)\ln(1-x)+x$	n/a	n/a
3D diffusion: Jander equation (D3)	$\{3(1-x)^{2/3}\}/\{2[1-(1-x)^{1/3}]\}$	$[1-(1-x)^{1/3}]^2$	n/a	n/a
Ginstling–Brounshtein (D4)	$3/\{2[(1-x)^{-1/3}-1]\}$	$1-(2x/3)-(1-x)^{2/3}$	n/a	n/a
Zero-order (F0)	1	x	$x=[-\alpha t/2\beta][\exp(-\beta t^2)-1]$	$x=[\alpha/2\beta t][\exp(\beta t^2)-1]$
First-order (F1)	$1-x$	$-\ln(1-x)$	$x=1-\exp\{[\alpha t/2\beta][\exp(-\beta t^2)-1]\}$	$x=1-\exp\{[-\alpha/2\beta t][\exp(\beta t^2)-1]\}$
Second-order (F2)	$(1-x)^2$	$(1-x)^{-1}-1$	$x=1-\{[-\alpha t/2\beta][\exp(-\beta t^2)-1]+1\}^{-1}$	$x=1-\{[\alpha/2\beta t][\exp(\beta t^2)-1]+1\}^{-1}$
Third-order (F3)	$(1-x)^3$	$1/2[(1-x)^{-2}-1]$	$x=1-\{[-\alpha t/\beta][\exp(-\beta t^2)-1]+1\}^{-1/2}$	$x=1-\{[\alpha/\beta t][\exp(\beta t^2)-1]+1\}^{-1/2}$

Dispersive kinetic models are provided only for the F-series (see text for details). n/a, not applicable.

The authors assume that the distributions of activation energies for various dispersive processes take the general functional form/shape of the Maxwell–Boltzmann (M–B) kinetic energy distribution due to the role of molecular dynamics in affecting the observed reaction kinetics; the distribution is 'concave-down' for heterogeneous systems (i.e. those producing acceleratory, sigmoid conversion versus time, *x*–*t*, curves—which are characterized by slower rates earlier in the conversion than towards the end) and 'concave-up' (i.e. inverted) for homogeneous systems (i.e. those producing deceleratory, sigmoid *x*–*t* curves—which are characterized by faster rates earlier in the conversion, post-induction period, than towards the end) [8,9]. [An example of a dispersive homogeneous solid-state conversion is the thermal decomposition of silver permanganate e.g. [8]; it is a process which yields products from a single, homogeneous reagent. Heterogeneous solid-state conversions, on the other hand, typically involve polymorphic transformations and crystallizations, i.e. systems which involve the formation a 'product' condensed phase from a homogeneous/dissolved 'reagent' phase.] In either case, these activation energy distributions ultimately define (mathematically) a time-dependent rate constant, which the authors believe can be approximated by a specific functional form, as will be discussed later. When the time-dependent rate constant is coupled with an assumed first-order mechanism for the conversion, the dispersive kinetic model equations of the authors' previous works are obtained (i.e. one for treating homogeneous conversions and one for use in heterogeneous applications [8,9]).

In this work, it is demonstrated that it may be possible to convert some of the traditional kinetic models shown in Table 1 into corresponding 'dispersive kinetic models', using the approach described above. Additionally, the application of these various dispersive models to the isothermal decomposition of the antibiotic, oxacillin, originally investigated by Rodante et al. [14–16], is shown. This particular conversion is of interest to the authors for three main reasons: (1) the data is 'complex' and it cannot be satisfactorily fit/interpreted using most of the traditional kinetic models, even in combination, (2) the *x*–*t* data is 'less sigmoidal' in appearance than any other data the authors have attempted to model with their dispersive kinetic equations previously (thus, it may provide a good test of the potential limitations of the proposed dispersive kinetic models) and (3) the solid-state thermal decomposition of oxacillin, unlike other compounds the authors have previously investigated [8,9], appears to proceed via a heterogeneous mechanism rather than a homogeneous one (from visually examining the shape of the *x*–*t* trends). Finally, by utilizing some recent results [9], the authors attempt to show, via graphical analysis, that the dispersive model equation for first-order heterogeneous processes (i.e. the model which is ultimately used to treat the oxacillin data) predicts a 'M–B-like' (i.e. asymmetric, '∩-shaped') distribution of activation energies, as a function of the extent of conversion. This is an important goal because such a finding would lend support to the fundamental assumption (i.e. in the derivation of the various dispersive kinetic model equations presented in this work) of the existence of such activation energy distributions in dispersive conversions.