



An innovative reaction model determination methodology in solid state kinetics based on variable activation energy



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ARTICLE INFO

Article history:

Received 4 December 2013

Received in revised form 19 March 2014

Accepted 21 March 2014

Available online 4 April 2014

Keywords:

Solid state kinetics

Reaction model

Variable activation energy

Pre-exponential factor

Multi-step reactions

ABSTRACT

Determination of appropriate reaction model(s) in solid state reactions has been confronting with serious discrepancies over the decades. The dilemma in the choice of reaction models originates from the use of facile methods to handle the complicated multi-step kinetics. In order to minimize these discrepancies, an advanced reaction model determination methodology is put forward which deals with variable energy of activation concept. This methodology is expected to fairly simulate single step as well as multi-step reaction kinetics. The fresh expressions for the well known reaction models under this methodology are derived and their validity conditions are discussed. The methods for determining pre-exponential factor(s) in single step and multi-step processes are also reviewed. The proposed methodology is experimentally verified by taking an experimental example of non-isothermal curing kinetics of the polyepoxy formation (by the reaction between DGEBA and an aliphatic diamine) under constant as well as variable energies of activation. The obtained results are compared and effectively interpreted. The precautions while using the said methodology and its prospective applications are also discussed.

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1. Introduction

A thermally stimulated process is one in which the system has to overcome a potential energy barrier in order to shift itself toward forward. The energy distribution along the relevant coordinates in such a system is known to be governed by Boltzmann statistics. If the processes occurring in solid state are taken into consideration, several prominent physical phenomena and chemical reactions fall in this category [1]. The kinetic modeling of these thermally activated phenomena/reactions simulates their reaction rates by parameterizing generally the two variables, i.e., degree of conversion ' α ' and temperature ' T ', by using the kinetic triplets which in turn, could probe inside those phenomena/processes. In case of solid state processes, this task is complicated as even an apparently simple process which is dealt macroscopically, may consist of a number of complex processes occurring simultaneously (parallel/consecutive or both) [1–3]. Unfortunately, to kinetically interpret these kinds of complicated processes, some

oversimplified methods are available in thermal analysis which can just partially fulfill the challenges of this field, regarding the prominent complexity of these processes. This statement is in accordance with the results obtained by ICTAC Kinetic Project and the demand to put critical emphasis on the development of new and advanced techniques by ICTAC Kinetic Committee [4–9].

Indeed, isoconversional methods are capable to provide some clues about the complexity of processes in terms of the variation in their energies of activation with the degree of conversion (also called E – α dependency). These estimations could be useful [10,11]; yet, the complete description of the process inevitably requires the determination of explicit reaction model for the process. It is a shortcoming that the well known reaction model determination methods which are envisaged reliable in this field are based upon either the single choice of activation energy (effective energy), the use of approximations or they focus on kinetic compensation principle whose origin is questionable [12–16]. Therefore, an attempt has been made to develop an advanced reaction model determination methodology based upon the concept of variable energy of activation. This approach may not only be helpful to determine the true pictures of reaction models in case of complex solid state processes but also it could provide basis to propose a number of new and relatively more elaborated reaction models.

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2. Theoretical basis of solid state kinetics

The extent of solid state reactions is effectively described by a term degree of conversion ' α ' and is defined as following:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (1)$$

where ' m_0 ' is the initial mass of reactant, ' m_t ' is its mass at certain time during the reaction and ' m_∞ ' is its mass at the end of reaction. For these reactions, the reaction rate $d\alpha/dt$ being the function of ' α ' can be described as

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

Eq. (2) is the basic kinetic equation of solid state mass loss reactions [1]. When isothermal/non-isothermal conditions are under considerations, ' k ' is often replaced by ' $k(T)$ ' whose value is substituted in Eq. (2) by Arrhenius equation which then takes the following form:

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

whence A is pre-exponential factor, E_α is the energy of activation and $f(\alpha)$ is a function of degree of conversion, called reaction model. Physically, A describes the collision frequency of particles involved in the formation of activated complex; E_α is the reaction's energy barrier and $f(\alpha)$ furnishes information about the mechanism of reaction(s). A combination of A , E_α and $f(\alpha)$ is known as the kinetic triplet [1,17,18]. Each and every member of kinetic triplet has its relevant complementary contribution to explain the whole physical phenomenon.

2.1. Pre-existing kinetic triplet evaluation methods

2.1.1. Estimation of activation energy by isoconversional methods

Isoconversional methods are based upon the isoconversional principle which states that: "at certain extent of conversion, the rate of a solid state reaction depends only upon the temperature" [1] as shown in Eq. (4):

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial(1/T)}\right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial(1/T)}\right]_\alpha + \left[\frac{\partial \ln f(\alpha)}{\partial(1/T)}\right]_\alpha \quad (4)$$

As α is constant, $f(\alpha)$ is also assumed constant. Under these conditions, Eq. (4) is reduced into Eq. (5) as following:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial(1/T)}\right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial(1/T)}\right]_\alpha = -\frac{E_\alpha}{R} \quad (5)$$

Eq. (5) provides basis to calculate the values of the activation energy in a model free way. However, thermally stimulated solid state processes are intrinsically multi-step with variable energy values. Even if E is apparently constant, there is still a probability that all kinds of participating reactions have nearly similar kinetic barriers or the overall kinetics is determined by a single step despite of the fact that it includes several steps [5,9]. As the reaction proceeds, its state alters with the degree of conversion. Therefore, the objective to treat Eq. (3) or its different integral forms under constant conditions of α is in fact, to estimate the variations in E_α at each value of α , which is one of the discriminating features of isoconversional kinetics. In case of non-isothermal kinetics, it is usually realized by using multiple heating rate programs. Isoconversional methods can be isothermal/non-isothermal, differential/integral and linear/nonlinear. They are named so because they may be inter-convertible by certain multiples arising from numerical differentiation or the integration of temperature integral and therefore generate nearly similar E - α dependency patterns [1].

By taking logarithm and rearranging Eq. (3) yields:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,\beta} = -\frac{E_\alpha}{RT_{\alpha,\beta}} + \ln\{Af(\alpha)\} \quad (6)$$

This expression is familiar well as Friedman's Method [19]. The E_α values can be determined by plotting $\ln(d\alpha/dt)$ against $1/T$ at certain values of ' α ' which inevitably demands numerical differentiation. As a result, this method generates significantly scattered reaction rates and therefore, irregular patterns of E_α values.

There is still a possibility to avoid the numerical differentiation by implying integral methods. So, integration of Eq. (3) results in:

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (7)$$

Say, if T_0 is low, it is suitable to suppose $\alpha_0=0$ and assuming that there is no reaction between 0 and T_0 . Eq. (7) then takes the following form:

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \left(\frac{A}{\beta}\right) I(E, T) \quad (8)$$

where $g(\alpha)$ is called the integrated reaction model in Eq. (8). In this equation, we confront with one of the crucial issues of thermal analysis namely temperature integral $I(E, T)$ [20] whose analytical solution is unavailable. The similar matters can however be handled alternatively by numerical analysis. A number of approximations applied to numerically solve the temperature integral yields the following generalized linear integral isoconversional method:

$$\ln\left(\frac{\beta}{T_a^b}\right) = \text{Const.} - \left(\frac{aE_\alpha}{RT_\alpha}\right) \quad (9)$$

In Eq. (9), ' a ' and ' b ' are constants and ' E_α ' is the energy of activation for an arbitrary linear integral isoconversional method. Eq. (9) can be rearranged in the following way:

$$\ln \beta - b \ln T_\alpha = \text{Const.} - \left(\frac{aE_\alpha}{RT_\alpha}\right) \quad (10)$$

Differentiation of Eq. (10) with respect to $1/T_\alpha$ provides the following equation:

$$\frac{d \ln \beta}{d(1/T_\alpha)} - b \frac{d \ln T_\alpha}{d(1/T_\alpha)} = -\frac{aE_\alpha}{R} \quad (11)$$

Eq. (11) can be written down in the following way:

$$E_\alpha = -\frac{R}{a} \left[\frac{d \ln \beta}{d(1/T_\alpha)} - b \frac{d \ln T_\alpha}{d(1/T_\alpha)} \right] \quad (12)$$

whence $d \ln \beta/d(1/T_\alpha)$ is the slope of straight line drawn between $\ln \beta$ and $1/T_\alpha$ at each value of ' α ' in Ozawa-Flynn-Wall (OFW) method [21] denoted by $(m_\alpha)_{\text{OFW}}$ and the graph between $\ln T_\alpha$ against $1/T_\alpha$ appears a straight at each value of ' α ' whose slope is denoted by $(m_\alpha)_T$. Eq. (12) then takes the following form:

$$E_\alpha = -\frac{R}{a} \{(m_\alpha)_{\text{OFW}} - b(m_\alpha)_T\} \quad (13)$$

Therefore, the energy of activation of any linear integral isoconversional method at any value of ' α ' can be determined by implying Eq. (13) provided that:

- (i) The values of the constants ' a ' and ' b ' are known.
- (ii) The values of ' $(m_\alpha)_{\text{OFW}}$ ' and ' $(m_\alpha)_T$ ' at the relevant values of ' α ' are known.

For instance $(a,b)=(1.052,0)$ for OFW method; $(a,b)=(1,2)$ in case of Kissinger-Akahira-Sunose (KAS) method [22] and $(a,b)=(1.0008, 1.92)$ in case of Starink's method [23], etc.

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