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Determination of pre-exponential factors and of the mathematical functions $f(\alpha)$ or $G(\alpha)$ that describe the reaction mechanism in a model-free way

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ABSTRACT

The study compared the accuracy of several model-fitting methods for the computation of compensation parameters. Two methods were presented for the model-free computation of the pre-exponential factor dependency using kinetic compensation parameters and isoconversional methods. These methods give accurate results for both single and multi-step kinetics. Once the pre-exponential factors have been evaluated in a model-free way, three model-free methods were proposed to compute the values of the mathematical function that describes the reaction mechanism for multi-step kinetics. These methods can be preferred according to the type of data available (i.e. differential or integral). Accurate results were obtained for both single and multi-step kinetics using two sets of simulated data and an experimental example.

1. Introduction

Isoconversional methods are amongst the more reliable kinetic methods for the treatment of thermoanalytical data, see for example [1–10]. The major information produced by these methods is the dependence of the apparent activation energy with the extent of conversion, called the E_α-dependency. This dependency is important for detecting and treating multi-step kinetics. On the other hand, the E_α-dependencies evaluated by isoconversional methods allow for meaningful mechanistic and kinetic analyses as well as for reliable kinetic predictions. One of the main advantages of these methods is that they provide a way of obtaining kinetic parameters without any assumption on the reaction mechanism. For this reason they are sometimes called "model-free". A direct consequence of this is that pre-exponential factors and kinetic exponents are not computed because this would inevitably require the knowledge of the reaction mechanism. This does not mean that it is not possible to compute these parameters using isoconversional analysis, but their determination will require making an assumption on the mathematical function used to describe the reaction mechanism.

Following the assumption that the reaction under study is complex and that the true reaction mechanism is unknown, an interesting way to compute the pre-exponential factor is to use the so-called compensation parameters. Because it is generally possible to find a false compensation effect between activation energy (E) and pre-exponential factor ($\ln A$), it is often possible to establish a (linear) relationship between these parameters. Then, the knowledge of this relationship, in association with the determination of the E_α-dependency obtained using an isoconversional method, gives a model-free estimation of the pre-exponential factor. Indeed, accurate values of the pre-exponential factor ($\ln A_\alpha$) can be estimated for single-step [11] and multi-step [12] processes from the E_α values obtained in a model-free way (i.e. by an isoconversional method), using this relationship.

The first objective of this work will be to compare the accuracy of various methods to compute activation energy, pre-exponential factors and compensation parameters. Then, new solutions will be given for the model-free determination of pre-exponential factors and of the mathematical function that describes the reaction mechanism. To the best of my knowledge, there is no other extensive study on the model-free determination of this function. Generally, the function that describes the reaction mechanism is selected amongst several pre-existing models as the one that gives the best fit of the data and the method is limited to single-step processes. The aim of this study is to propose a completely different methodology for the determination of this function for multi-step kinetics. This function is of great interest because it reflects the overall reaction mechanism of the transformation as measured by thermoanalytical techniques.

2. Theoretical approaches

The general form of the basic rate equation is usually written as [13]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

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α is the extent of conversion, t the time, T the temperature, $f(\alpha)$ is the mathematical function that represents the reaction mechanism and $k(T)$ is the rate coefficient, generally called rate constant.

2.1. Dependence of the rate coefficient with temperature

The dependence of the rate coefficient with temperature is given by the Arrhenius law [14]:

$$k(T) = A\,e^{-E/RT} \tag{2}$$

E is the activation energy, A the pre-exponential factor (in s^{-1}) and R the universal gas constant.

2.2. Isoconversional principle

Isoconversional methods are based on the isoconversional principle, stating that the reaction rate at constant extent of conversion is only a function of temperature [15]. According to Eq. (1)

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_\alpha + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_\alpha \tag{3}$$

henceforth the subscript α indicates the values related to a given extent of conversion. Within the basic assumption of isoconversional methods $f(\alpha)$ does not depend on T, when α is constant, hence:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = -\frac{E_\alpha}{R} \tag{4}$$

As seen from Eq. (4), a model-free value of the apparent activation energy E_α can thus be estimated for each α value.

2.3. Nonisothermal isoconversional methods

2.3.1. Differential method of Friedman

From Eq. (1) we get:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{5}$$

This method is known as Friedman's method [16]. Application of this method requires the knowledge of the reaction rate $(d\alpha/dt)_{\alpha,i}$ and of the temperature $T_{\alpha,i}$ corresponding to a given extent of conversion, for the i temperature programs used. In this study, a value of E_α was computed for each value of α lying in between 0.01 and 0.99 with a step of 0.01. The advantages of differential methods such as Friedman's method are that they make no approximations and can be applied to any temperature program. This does not hold for usual integral methods. Nevertheless, simulations have shown that differential isoconversional methods can sometimes reveal numerical instability in regard to integral one, care must be taken if the reaction heat varies noticeably with the temperature program [17] and their accuracy can be limited due to baselines determination limit for real experimental data [18].

2.3.2. Integral methods

2.3.2.1. Classical methods. Using a linear temperature program $\beta = dT/dt$ Eq. (1) is written [19,20]:

$$\frac{d\alpha}{dT} = \frac{k(T)f(\alpha)}{\beta} \tag{6}$$

and

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

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

which does not have an analytical solution. If E/RT is replaced by x and integration limits transformed, Eq. (8) becomes [21]

$$g(\alpha) = \frac{AE}{R\beta}\int_0^\infty \frac{\exp(-x)}{x^2}dx \tag{9}$$

where $x = E/RT$ is the reduced activation energy at the temperature T. The function $p(x)$ can be replaced by a number of useful approximations, which have been discussed by Flynn [22]. Note that Eq. (9) assumes a constant value of E. It was shown that for strong variations of E_α with α, this assumption is the main source of errors of integral methods and explains the differences obtained between integral and differential isoconversional methods [23]. This statement has clearly shown the necessity of developing advanced isoconversional methods taking into account for the E_α variation in the computational procedures. For a detailed comparison of the accuracy of integral methods see Refs. [18,24].

2.3.2.2. Advanced isoconversional method or Vyazovkin's method. To overcome the drawbacks of integral methods and to take into account for the variation of E in the computation of the temperature integral, an advanced isoconversional method has been developed.

According to Eq. (1)

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A\int_0^t \exp\left[-\frac{E}{RT(t)}\right]dt \tag{10}$$

$$g(\alpha) = AJ[E,\ T_i(t)] \tag{11}$$

The E_α value is determined as the value that minimizes the function [25,26]

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \tag{12}$$

where J is evaluated over small intervals to take into account for the variation of E

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right]dt \tag{13}$$

This method is applicable to any temperature program and uses a numerical integration of the temperature integral. The resulting advanced isoconversional method allows one to handle a set of n experiments carried out under different arbitrary temperature programs, $T_i(t)$.

The software developed by Sbirrazzuoli [17] was used to compute a value of E_α for each value of α lying in between 0.01 and 0.99 with a step of 0.01. In this software, numerical integration is performed using trapezoidal rule. An accurate interpolation of the integrated $\alpha - T$ curves is performed using a Lagrangian algorithm to find the time $t_{\alpha,i}$ and temperature $T_{\alpha,i}$ that correspond to a given α for the i temperature programs used. The precision on the determination of the time to reach a given α value can be extended for very fast temperature programs as was recently done for Fast Scanning Calorimetry (FSC) [27]. Several possibilities are proposed in this software for the initial estimate E_0 of E_α in the non-linear procedure. The first possibility is based on the assumption that $\Phi(E_\alpha)$ can be approximated by a quadratic parabola with an interval of variation of E_α typically lying in between 1 and 400 kJ mol^{-1} as initially proposed by Vyazovkin [25]. On the other hand, it is also possible to use the E_α values obtained by Friedman method as an initial estimate of E_α or an iterative computational procedure between extreme values (−5000 and +5000 kJ mol^{-1} for example). This last procedure has been developed to be applicable to strong E_α variations and apparent negative variations as observed in the case of crystallization of thermoplastics (anti-Arrhenian behavior) [28]. This non-linear method (NLN Vyazovkin) was applied in this study.