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Reducing the effects of noise in the calculation of activation energy by the Friedman method

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ABSTRACT

The Friedman method for analysis of kinetic parameters of solid-state reactions has been widely used. One of the drawbacks of this method is its sensitivity to noise which can be caused by both experimental error and the intrinsic inaccuracy of the differential methods, particularly for non-isothermal kinetic data obtained by means of thermogravimetric analysis (TGA). This paper proposes a modified version of the Friedman method in order to decrease the effect of noise and consequently obtain more accurate activation energy values. The new method is based on the idea of considering, for a given value of the extent of conversion α, not only information corresponding to α but also data in its neighbourhood. To check the procedure, it is applied to simulated data and the activation energy obtained is compared with the preset value and that given by the Friedman method. Moreover, the proposed method is used to determine the activation energy on the thermal degradation of γ-Ti(PO_4)(NH_4HPO_4) compound as a function of the extent of conversion.

1. Introduction

Thermal analysis techniques have been used since the 20th century to study solid-state reactions and they have been revealed as a useful tool in obtaining the kinetic parameters of reactions involving weight or enthalpy change by using a small amount of sample. Weight loss data are converted to a normalized form called extent of conversion α, which ranges from 0 to 1 and it is a measure of the reaction progress as a function of time or temperature.

For non-isothermal thermogravimetric analysis, the extent of conversion at any temperature is

$$\alpha = \frac{m_0 - m_T}{m_0 - m_\infty} \tag{1}$$

where m_T represents the sample mass at temperature T, and m_0 and m_∞ are the sample mass at the beginning and at the end of the process, respectively.

The theory concerning kinetic analysis is based on the differential equation [1]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where $k(T)$ is the temperature-dependent rate and $f(\alpha)$ is the reaction model function, which is related to the mechanism of the process.

The temperature dependence of the reaction rate solid-state function is usually given by the Arrhenius equation [2]

$$k(T) = A\exp\left(\frac{-E}{RT}\right) \tag{3}$$

where A is the pre-exponential factor (frequency), E is the activation energy and R is the gas constant. Then, Eq. () turns into

$$\frac{d\alpha(t)}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha(t)) \tag{4}$$

The experimental data for studying the kinetic behavior of thermally stimulated solid reactions obtained at several constant temperatures are considered in isothermal methods, and those involving heating samples at one or more heating rates are included in non-isothermal

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(dynamic) methods. Usually, non-isothermal methods employ a constant heating rate β, in which the temperature changes linearly with the time:

$$T = T_0 + \beta t \tag{5}$$

Replacing temporal derivative with a temperature derivative, Eq. (4) turns into

$$\frac{d\alpha(T)}{dT} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right) f(\alpha(T)) \tag{6}$$

The determination of *A*, *E* and f(α), the so-called kinetic triplet, is an interlinked problem. An important number of mathematical methods have been developed to evaluate solid-state kinetics and to get the kinetic parameters from thermal experiment data. They generally fall into two categories: model-fitting and isoconversional methods. Model-fitting methods consider a particular reaction model function which is assumed to represent the conversion dependence on the reaction rate. This assumption is not necessary in isoconversional methods and, for this reason, they are also named model-free methods.

Isoconversional methods require several kinetic curves at different temperature programs to perform the analysis and they have therefore been called multi-curve methods [3]. For a fixed value of extent of conversion α, thus the name isoconversional, calculation from several curves at different heating rates are performed obtaining a plot of the activation energy versus the extent of conversion.

Isoconversional methods can be divided into integral and differential methods [4,5]. The first ones may lead to significant mistakes in the activation energy values due to the fact that some approximations are necessary for estimation of the temperature integral [6]. The most popular isoconversional integral methods are the Ozawa–Flynn–Wall (OFW) [7,8], Kissinger–Akahira–Sunose (KAS) [9–11] and Ortega [12] methods, which are based on approximations of the temperature integral and they are limited to the use of a linear variation of the temperature. Over the years, advances in computational software have made it easier for different kind of methods to avoid the temperature integral approximation, although a more computational effort is required. For instance, the non-linear method proposed by Vyazovkin [13,14] or the iterative procedure introduced by Cai [15].

One of the main sources of inaccuracy in the differential methods is its sensitivity to noise [4,12]. It is due to the fact that the value of the activation energy is obtained from Eq. (6), where only data corresponding to a fixed value of the extent of conversion α for the different heating rate programs are involved. Consequently, imprecision in the determination of temperatures or process rates may introduce significant differences between the right and the calculated values, in particular when a small number of runs is considered. This imprecision may be caused both by experimental noise or/and by intrinsic inaccuracy of the differential methods. On the one hand, significant inaccuracy can be introduced when differential experimental data, such as DTA and DSC, are considered because of the difficulty in determining the baseline. On the other hand, when integral experimental data are considered, such as TGA, numerical differentiation is necessary to obtain the extent of conversion rate.

Friedman proposed a method [16] that is included in the family of differential isoconversional methods. It has been widely used and is one of the simplest procedures to obtain the activation energy. Taking logarithms in Eq. (4), we get

$$\ln\left(\frac{d\alpha(t)}{dt}\right) = \ln(A\ f(\alpha(t))) - \frac{E}{RT} \tag{7}$$

Considering several runs for different constant heating rates β_i and for a given value of α, Eq. (7) leads to

$$\ln\left(\frac{d\alpha(T)}{dT}\beta_i\right) = \ln(A\ f(\alpha(T))) - \frac{E}{RT} \tag{8}$$

and thus, since ln(A f(α(T))) is independent of β_i, the points

$$\left(\frac{1}{T_{\alpha,i}},\ \ln\left(\frac{d\alpha(T)}{dT}\beta_i\right)\right) \tag{9}$$

are in the same straight line. Hence, by fitting the experimental data, the activation energy *E* can be obtained. Although constant heating rates have been considered, this relation also holds for any temperature heating program changing β by the temperature derivative.

The aim of the present research is to propose an improvement on the isoconversional differential Friedman (FR) method. More specifically, we introduce a procedure to reduce the uncertainty in the values of the activation energy by the FR method. This procedure is applied to two simulated models and the results by both the FR and the modified Friedman (MFR) methods are compared. In addition, the kinetic study of a practical case is performed.

2. Methods

The influence of noise in the Friedman method could be reduced if information corresponding to a value of α is the only data considered. For this purpose, given a fixed value of α, set $\alpha_j = \alpha, \alpha_{j-1} = \alpha - \Delta\alpha, \alpha_{j+1} = \alpha + \Delta\alpha$. For each $k = j-1, j, j+1$ and for *n* constant heating programs of temperature β_i, Eq. (8) leads to

$$\ln\left(\frac{d\alpha(T_{k,i})}{dT}\beta_i\right) = \ln(A\ f(\alpha_k)) - \frac{E}{RT_{k,i}} \tag{10}$$

Assuming the activation energy *E* is constant or, if it were not the case, variations of *E* over the interval $[\alpha_{j-1}, \alpha_{j+1}]$ can be neglected, this means the points

$$\left(\frac{1}{T_{k,i}},\ \ln\left(\frac{d\alpha(T_{k,i})}{dT}\beta_i\right)\right) \tag{11}$$

belong to three different straight lines r_k but note they are parallel and their slopes are exactly the same, ${}^{-E}/_{R}$. Thus, we can try to find this slope by fitting the data for all these points simultaneously. So we are looking for four numbers *m*, n_1, n_2, n_3 minimizing the function

$$h(m, n_1, n_2, n_3) = \sum_{k=j-1}^{j+1}\sum_{i=1}^{n}(y_{k,i} - m x_{k,i} - n_k)^2 \tag{12}$$

where $y_{k,i} = \ln\left(\frac{d\alpha(T_{k,i})}{dT}\beta_i\right)$, $x_{k,i} = \frac{1}{T_{k,i}}$ and $n_k = \ln(A\ f(\alpha_k))$.

This algorithm, as all computations in this study, has been implemented in MatLab and the built-in function fminsearch has been used to find the minimum. Naturally, in the hopes of getting better results, more points can be considered, for instance, $\alpha_{j-2}, \alpha_{j-1}, \alpha_j, \alpha_{j+1}, \alpha_{j+2}$. The implementation in this case is similar to the previous one.

3. Results and discussion

To validate the modification of the FR method that has been proposed for calculation of activation energy, it was applied to both simulated and experimental data.

3.1. Simulation data

Firstly, a theoretical model corresponding to a single-step reaction given by $f(\alpha) = 1 - \alpha$, $E = 100$ kJmol^{-1} and $A = 10^9$ min^{-1} was