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Short Communication

NON-ISOTHERMAL KINETICS IN SOLIDS

The precision of some integral methods for the determination of the activation energy without neglecting the temperature integral at the starting temperature

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The integral methods, which are obtained from the various approximations for the temperature integral, have been extensively used in the non-isothermal kinetic analysis. In order to obtain the precision of the integral methods for the determination of the activation energy, several authors have calculated the relative errors of the activation energy obtained from the integral methods. However, in their calculations, the temperature integral at the starting temperature was neglected. In this work, we have performed a systematic analysis of the precision of the activation energy calculated by the integral methods without doing any simplifications.
The results have shown that the relative error involved in the activation energy determined from the integral methods depends on two dimensionless quantities: the normalized temperature $\theta=T/T_0$, and the dimensionless activation energy $x_0=E/RT_0$ (where E is the activation energy, T is the temperature, T_0 is the starting temperature, R is the gas constant).

Keywords: *activation energy, integral method, non-isothermal kinetics, temperature integral*

Introduction

In the mathematical analysis of non-isothermal thermoanalytical data, the calculation of the temperature integral has been usually involved [1]. Due to the fact that there is no closed form solution of the temperature integral, different approximated equations have been proposed [2–5]. The main application of these proposed approximations is the determination of the kinetic parameters, in particular the activation energy, and not the computation of the temperature integral [6]. It would be interest to estimate the precision of the integral methods for the determination of the activation energy. Several authors have carried out the systematic analysis of the relative error involved in the activation energy obtained from the integral methods in their papers [6–13]. However, the temperature integral at the starting temperature was neglected in their calculations. Recently, we analyzed the precision of one type integral methods, which is based on the temperature integral approximations as the form, for the determination of the activation energy without neglecting the low temperature end of the temperature integral [14]. Cai and Bi [15] performed the systematic analysis of the precision of Coats and Redfern method for the determination of the activation energy without neglecting the low temperature end of the temperature integral. The aim of this paper is to perform an analysis of the relative error involved in the activation energy computed from some integral methods without doing any simplification. The integral methods analyzed in this paper include the Fischer–Jou–Gokalgandhi method [16], the Gorbachev method [17], the Wanjun–Yuwen–Hen–Zhiyong–Cunxin method [18], the Cai–Yao–Yi–He method [19], and the Cai-He method [20], which are extensively used in the kinetic analysis of solid-state reactions.

Theory

The rate of thermally stimulated solid-state reactions depends on the temperature and the extent of reaction [21]. If only a single reaction is involved, it is usually assumed that these functions are separable and the equation used to described the progress of reaction is

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

where α is the extent of reaction, t is the time, T is the temperature, $k(T)$ is the rate constant depending on the temperature and $f(\alpha)$ is the kinetic function which is related to the reaction mechanism.

The rate constant is normally expressed by the Arrhenius equation

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

where A is the frequency factor, E is the activation energy and R is the gas constant.

Equation (2) is inserted in Eq. (1), therefore

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\mathrm{e}^{-E/RT}f(\alpha) \tag{3}$$

The most common heating profile used for studying solid-state reactions is the linear heating program ($T=T_0+\beta t$, where β is the heating rate and T_0 is the starting temperature) [6]. For linear heating conditions, Eq. (3) may be written as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\mathrm{e}^{-E/RT}f(\alpha) \tag{4}$$

By separation of variables and integration, one can get

$$g(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_0}^{T}\mathrm{e}^{-E/RT}\mathrm{d}T \tag{5}$$

On the basis of Eq. (5), it is possible to analyze the experimental data by the integral methods, in order to determine the kinetic parameters. However, the integral in the right-hand side has no exact analytical solution and many approximations are generally used. In all of them it is considered that the value of the integral between 0 and T_0 is negligible [22]. In this case

$$g(\alpha)=\frac{A}{\beta}\int_0^{T}\mathrm{e}^{-E/RT}\mathrm{d}T \tag{6}$$

This integral is called the temperature integral [23], which can be approximated in different ways. The most common of them lead to expressions of the type [24]:

$$g(\alpha)=\frac{A}{\beta}\frac{RT^2}{E}\mathrm{e}^{-E/RT}h(x) \tag{7}$$

where $x=E/RT$ and $h(x)$ is a function whose value is as closer to unity as higher is x and many particular forms, depending on the technique of approximation. The common and extensively used forms of the $h(x)$ function are listed in Table 1.

Therefore,

$$g(\alpha)=\frac{A_\mathrm{a}}{\beta}\frac{RT^2}{E_\mathrm{a}}\mathrm{e}^{-E_\mathrm{a}/RT}h(x_\mathrm{a}) \tag{8}$$

In the above equation, the subscript a stands for the apparent values of the kinetic parameters obtained from the above integral method and $x_\mathrm{a}=E_\mathrm{a}/RT$.

If the integral method were used for performing the kinetic analysis, the apparent activation energy, E_a, would be obtained from the slope of the plot of $\ln[g(\alpha)/T^2]$ *vs.* $1/T$:

$$\frac{\mathrm{d}\ln[g(\alpha)/T^2]}{\mathrm{d}(1/T)}=-\frac{E_\mathrm{a}}{R}\left(1-\frac{\mathrm{d}\ln h(x_\mathrm{a})}{\mathrm{d}x_\mathrm{a}}\right) \tag{9}$$

Equation (5) may be rendered dimensionless by normalizing the temperatures by the starting temperature and defining a new variable $\theta=T/T_0$. Then

$$g(\alpha)=\frac{AT_0}{\beta}\int_1^\theta\mathrm{e}^{-x_0/\theta}\mathrm{d}\theta \tag{10}$$

where $x_0=E/RT_0$.

Equation (10) is structurally similar to Eq. (5), but has the advantage of setting the lower value of the integration interval without doing any simplification (as $T_0=0$). The integral presented in Eq. (10) depends only on two dimensionless quantities (the parameter x_0 and the normalized temperature θ).

The real value of the left hand side of Eq. (9) can be determined from Eq. (10):

$$\frac{\mathrm{d}\ln[g(\alpha)/T^2]}{\mathrm{d}(1/T)}=\frac{E}{R}\left[\frac{2\theta}{x_0}-\frac{\theta^2}{x_0}\frac{\mathrm{d}\ln\left(\int_1^\theta\mathrm{e}^{-x_0/\theta}\mathrm{d}\theta\right)}{\mathrm{d}\theta}\right] \tag{11}$$

Table 1 Some forms of the $h(x)$ function

	$h(x)$
Fischer–Jou–Gokalgandhi [18]	1
Coats-Redfern [19	$(x-2)/x$
Gorbachev [20]	$x/(x+2)$
Wanjun–Yuwen–Hen–Zhiyong–Cunxin [21]	$x/(1.00198882x+1.87391198)$
Cai–Yao–Yi–He [22]	$(x+0.66691)/(x+2.64943)$
Cai–He [23]	$(0.99962x+0.60642)/(x+2.56879)$

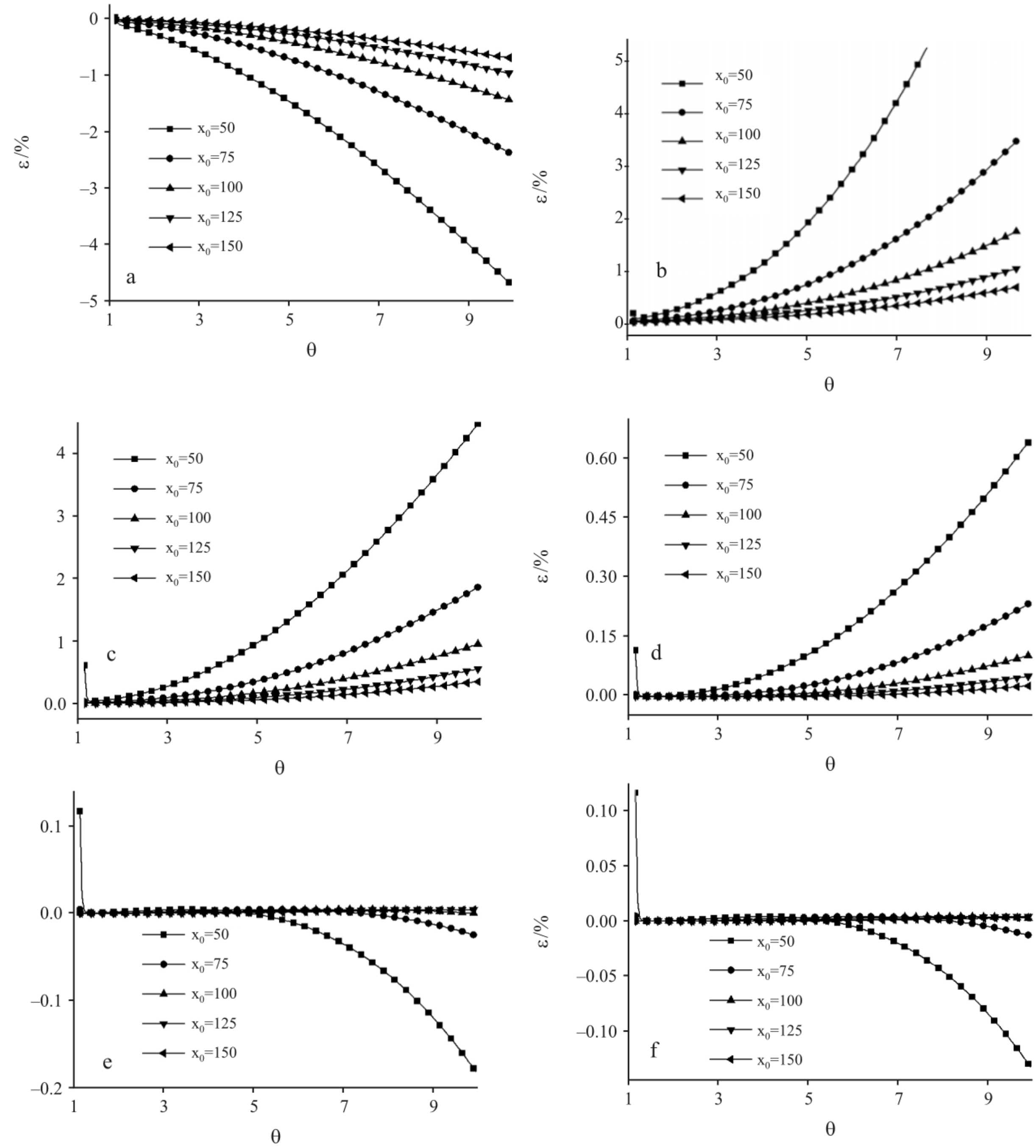

Fig. 1 Values of the relative error for the activation energy calculated by the integral methods as a function of the parameters x_0 and θ; a – Fischer–Jou–Gokalgandhi; b – Coats–Redfern, c – Gorbachev; d – Wanjun–Yuwen–Hen–Zhiyong–Cunxin; e – Cai–Yao–Yi–He; f – Cai–He

Here, we define the relative error of the activation energy

$$\varepsilon = \frac{E_a - E}{E} \tag{12}$$

From Eq. (12), it follows

$$x_a = (\varepsilon + 1)\frac{x_0}{\theta} \tag{13}$$

Therefore, the equation of ε can be obtained from Eqs (9), (11)–(13):

$$-(\varepsilon+1)\left\{1 - \frac{\mathrm{d}\ln h[(\varepsilon+1)x_0/\theta]}{\mathrm{d}[(\varepsilon+1)x_0/\theta]}\right\} = \frac{2\theta}{x_0} - \frac{\theta^2}{x_0}\frac{\mathrm{d}\ln\left(\int_1^\theta e^{-x_0/\theta}\mathrm{d}\theta\right)}{\mathrm{d}\theta} \tag{14}$$

Equation (14) indicated that the values of ε depend on two dimensionless quantities: x_0 and θ, and therefore, on the value of the activation energy, the starting temperature and the range of temperature of the process.

Results and discussion

The values of ε for the different values of x_0 and θ have been calculated by means of the Mathematica software system, which can perform the symbolic calculation as well as the numerical analysis [25]. The resulting ε values as a function of the parameters x_0 and θ are shown in Fig. 1. The values shown in Fig. 1 illustrate that there is a significant influence of x_0 and θ in the precision of the calculated activation energy values.

Conclusions

The integral methods which use the approximations of the temperature integral are generally reliable methods for the calculation of activation energies of thermally stimulated reactions studied during linear heating. These methods generally neglect the temperature integral at the starting temperature. A systematic analysis of the relative error of the activation energy calculated by some integral methods has been carried out. Our results have shown that the relative errors of the activation energy obtained from the integral method depend on two parameters: $x_0=E/RT_0$ and $\theta=T/T_0$.

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