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Short Communication

ON EVALUATE OF THE INTEGRAL METHODS FOR THE DETERMINATION OF THE ACTIVATION ENERGY

J. M. Cai[*] *and R. H. Liu*[**]

School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

Recently, Órfão obtained two simple equations for the estimation of the relative error in the activation energy calculated by the integral methods [2]. In this short communication, the validity of the equations has been evaluated by comparing the results calculated by the equations with the results calculated by the equation from theoretical derivation without introducing any assumption.

Keywords: *activation energy, integral methods, non-isothermal kinetics*

Introduction

As the temperature integral does not have an exact analytical solution, different approximations have been proposed in the literature. A large number of approximated equations have been proposed with the objective of increasing the precision in the determination of the temperature integral, as checked from the standard deviation of the approximations with regard to the real exact value of the temperature integral.

However, the main application of these approximations for the temperature integral is the determination of the kinetic parameters, in particular the activation energy, and not the computation of the temperature integral. Based on these approximations, the corresponding integral methods have been obtained in order to determine the activation energy. Therefore, it would be interesting to estimate the precision of the integral methods for the determination of the activation energy [1].

In his review paper recently published in AIChE Journal, Órfão [2] analyzed the precision of the integral methods for the determination of the activation energy and obtained two simple equations for the estimation of the relative error in the activation energy calculated by the integral methods.

The aim of this short communication is to verify the validity of the equations proposed by Órfão [2].

Relative error in the activation energy

The integral form of the kinetic equation for solid-state reactions can be written as follows:

$$g(\alpha)=\frac{A}{\beta}\int_{0}^{T}e^{-E/RT}\mathrm{d}T \tag{1}$$

where $g(\alpha)$ is the integral conversion function.

By introducing the variable $x=E/RT$, one can obtain

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

where

$$Q(x)=x^2e^x\int_{x}^{\infty}\frac{e^{-x}}{x^2}\mathrm{d}x \tag{3}$$

The $Q(x)$ function does not have an exact solution, and can be numerically calculated. The numerical values of the $Q(x)$ function as a function of the parameter x are shown in Fig. 1. The numerical integration has been performed by means of the Mathematica software developed by Wolfram Research, Inc. [3].

If the integral methods were used for performing the kinetic analysis of solid-state reactions, the apparent activation energy, E_a, would satisfy the following equation:

$$g(\alpha)=\frac{A_a}{\beta}\frac{RT^2}{E_a}h(x_a)e^{-E/RT} \tag{4}$$

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[*] Author for correspondence: jmcai@sjtu.edu.cn

[**] Author for correspondence: liurhou@sjtu.edu.cn

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

where the subscript a stands for the apparent values of the kinetic parameters obtained from the integral methods, $h(x)$ is the approximation for the $Q(x)$ function and $x_a=E_a/RT$.

From Eq. (4), it follows:

$$\frac{\mathrm{d}\ln[g(\alpha)/T^2]}{\mathrm{d}(1/T)}=-\frac{E_a}{R}\left(1-\frac{\mathrm{d}\ln h(x_a)}{\mathrm{d}x_a}\right) \tag{5}$$

The real value of the left hand side of Eq. (5) as a function of the true activation energy, E, can be determined from Eq. (2):

$$\frac{\mathrm{d}\ln[g(\alpha)/T^2]}{\mathrm{d}(1/T)}=-\frac{E}{R}\left(1-\frac{\mathrm{d}\ln Q(x)}{\mathrm{d}x}\right) \tag{6}$$

We define the relative error of the apparent activation energy ε:

$$\varepsilon=\frac{E_a-E}{E} \tag{7}$$

From Eq. (7), one can obtain

$$x_a=(\varepsilon+1)x \tag{8}$$

From Eqs (5)–(8), it follows:

$$(\varepsilon+1)\left(\frac{\mathrm{d}\ln h[(\varepsilon+1)x]}{\mathrm{d}[(\varepsilon+1)x]}\right)=1-\frac{\mathrm{d}\ln Q(x)}{\mathrm{d}x} \tag{9}$$

Órfão [2] put forward two simple equations for the estimation of the relative error in the apparent activation energy calculated by means of the integral methods:

$$\varepsilon=\frac{\mathrm{d}\ln h(x)}{\mathrm{d}x}-\frac{\mathrm{d}\ln Q(x)}{\mathrm{d}x} \tag{10}$$

$$\varepsilon=(\varepsilon+1)\frac{\mathrm{d}\ln h(x)}{\mathrm{d}x}-\frac{\mathrm{d}\ln Q(x)}{\mathrm{d}x} \tag{11}$$

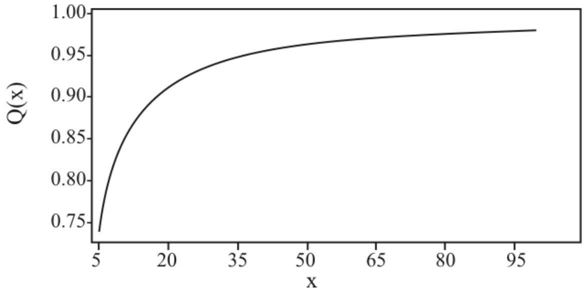

Fig. 1 Numerical values of $Q(x)$ at various x

Table 1 The precision of the Coats and Redfern method for the determination of the activation energy calculated from three different equations

x	Real value/%	Calculated by Eq. (10) ε/%	Calculated by Eq. (10) Deviation from real valve/%	Calculated by Eq. (11) ε/%	Calculated by Eq. (11) Deviation from real valve/%
5	7.15007	18.09688	153.101	20.88101	192.0394
10	0.99939	3.96977	297.220	4.07156	307.4048
15	0.30924	1.73840	462.155	1.75641	467.9802
20	0.13395	0.97634	628.894	0.98179	632.9665
25	0.069824	0.62556	795.913	0.62775	799.0405
30	0.040938	0.43515	962.950	0.43619	965.4865
35	0.026037	0.32024	1129.949	0.32079	1132.083
40	0.017579	0.24556	1296.905	0.24588	1298.746
45	0.012424	0.19428	1463.821	0.19448	1465.439
50	0.0091035	0.15756	1630.702	0.15769	1632.146
55	0.0068692	0.13035	1797.555	0.13044	1798.858
60	0.0053105	0.10963	1964.385	0.10969	1965.572
65	0.0041900	0.093488	2131.195	0.093534	2132.285
70	0.0033640	0.080668	2297.988	0.080702	2298.996
75	0.0027416	0.070317	2464.767	0.070342	2465.705
80	0.0022639	0.061838	2631.535	0.061858	2632.411
85	0.0018910	0.054806	2798.293	0.054821	2799.115
90	0.0015957	0.048909	2965.042	0.048921	2965.816
95	0.0013589	0.043915	3131.783	0.043925	3132.515
100	0.0011667	0.039649	3298.518	0.039658	3299.212

Results and discussion

Equation (9) for the relative error of the apparent activation energy can not be analytically solved. But for a certain x value, Eq. (9) can be solved by some numerical techniques. For this purpose, either general purposed mathematical software or a computer program developed in any programming language is used. In this short communication, the Mathematica software has been used for numerical calculation of Eq. (9).

Among the existed integral methods, the most commonly used in the kinetic analysis of solid-state reactions is the integral method proposed by Coats and Redfern [4] (here called the Coats and Redfern method), although the method was proposed 50 years ago. In fact, for the original paper of Coats and Redfern, we have found about 2500 citations in the kinetic analysis of solid-state reactions (this information was obtained from the ISI web of Science database [5]).

The precision of the Coats and Redfern method for the determination of the activation energy has been calculated using Eqs (9)–(11). The obtained results have been given in Table 1.

From the results included in Table 1, it can be seen that the results calculated from Eq. (9) significantly differ from the results from two equations presented in the paper of Órfão [2]. Therefore, the simplified Eqs (10) and (11) are not proper to calculate the precision of integral methods.

Conclusions

In this short communication, a mathematical analysis has been performed for the estimation of the precision of the integral methods for the determination of the activation energy, which describes the relative error in the apparent activation energy. The results have shown that the relative error in the activation energy is dependent on the dimensionless quantity $x=E/RT$. Órfão proposed two simple equations for the estimation of the precision of the integral methods. However, the results calculated by the Órfão's equations significantly deviate from the real ones.

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