ERROR EVALUATION OF INTEGRAL METHODS BY CONSIDERATION ON THE APPROXIMATION OF TEMPERATURE INTEGRAL

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In this paper, the integral methods in general use are divided into two types in terms of their different ways to in order to deal with the temperature integral $p(x)$: for Type A the function $h(x)=p(x)x^2e^x$ is regarded as constant *vs. x*, while for Type B $h(x)$ varies *vs. x* and $\ln[p(x)]$ is assumed to have the approximation form of $\ln[p(x)]=a\ln x+bx+c$ (the coefficients *a*, *b*, and *c* are constant). The errors of kinetic parameters calculated by these two types of methods are derived as functions of *x* and analyzed theoretically. It is found that Type A methods have the common errors of activation energy, while the Coats-Redfern method can lead to more accurate value of frequency factor than others. The accuracy of frequency factor can be further enhanced by adjusting the expression of the Coats-Redfern approximation. Although using quite simple approximation of the temperature integral, the Coats-Redfern method has the best performance among Type A methods, implying that usage of a sophisticated approximation may be unnecessary in kinetic analysis. For Type B, the revised MKN method has a lower error in activation energy and an acceptable error in frequency factor, and thus it can be reliably used. Comparatively, the Doyle method has higher error of activation energy and great error of the frequency factor, and thus it is not recommended to be adopted in kinetic analysis.

Keywords: error evaluation, kinetic analysis, temperature integral

Introduction

Thermal analysis techniques such as thermogravimetry (TG) and differential scanning calorimetry (DSC) have been widely used to study the kinetics and mechanism of solid thermal decomposition reactions, generally carried out under a linear temperature program. The kinetic triplet (activation energy *E*, frequency factor *A* and kinetic model) can be derived from the experimental data based on the kinetic equation of solid-gas phase decomposition as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E/RT) f(\alpha) \qquad (1)$$

where $\alpha (0<\alpha<1)$ is the fractional conversion, ß (K min^{-1}) the heating rate, *E* (kJ mol^{-1}) the activation energy, *A* (min^{-1}) the pre-exponential factor, and *R* the gas constant. *T*(K) is the absolute temperature. The specific form of $f(\alpha)$ represents the hypothetical model of the reaction mechanism. Approaches to extract the kinetic triplet from the above expression can be generally divided into two categories according to the kind of data used, i.e. differential method by usding derivative thermogravimetry (DTG) data and integral method using TG data.

For integral methods, integrating Eq. (1) and substituting $x=E/RT$ for *T* gives:

$$G(\alpha) = \frac{AE}{\beta R} p(x) \qquad (2)$$

where $G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}, \quad p(x) = \int_\infty^x \frac{-e^{-x}}{x^2} dx$

here $p(x)$ is the Arrhenius temperature integral. Although the integral methods are believed to be more reliable and accurate than the differential methods [1], the temperature integral has been a subject of much concern and controversy for a long time, since it cannot be analytically integrated. Many authors have proposed extensive approximations of $p(x)$ with different mathematical complexities and numerical precisions [2–13], and the researchers were always seeking to prove how closely their formulae approach the precise values of $p(x)$. Flynn [14] provided a review on the various approximate expressions for the

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temperature integral, in which he reappraised the accuracies and utilities of these approximations according to their percentage deviations. In a recent paper, Heal [15] proposed an accurate method to evaluate the temperature integral by a series of Chebyshev polynomials. More recently, Tang *et al*. [16] also presented a precise formula for the temperature integral by using two-step linear fitting process. Moreover, some papers proposed a kind of approximations of $p(x)$ through integration over small temperature intervals to enhance the accuracy [17–20].

Sestak ever presented a good discussion on the applicability of the $p(x)$-function in the kinetic analysis under non-isothermal conditions [21]. In the evaluation of the temperature integral, an important point is that it should not be regarded as a pure mathematical problem, but should be considered in connection with the aim of kinetic analysis, i.e. accurate extraction of kinetic parameters and model description. Any approximation leading to accurate enough evaluation of the kinetic parameters should be regarded as reasonable. In this sense, some approximations with higher mathematical complexities may have no remarkable advantage over some other simple approximations. With this idea in mind, in this paper we propose a new consideration on the published approximations and compare them by examining their performances in kinetic analysis, whereby the integral methods are evaluated and compared in terms of error analysis.

Theoretical consideration

Before the error analysis of integral methods, we first propose a new classification of the methods to divide them into two types. The error analysis will be conducted in section 3 respectively with regard to the two types.

It is known that besides $p(x)$, another function $h(x)$ introduced by Senum and Yang [12] can also be used to express the integral form (2) as follows:

$$G(\alpha) = \frac{AE}{\beta R} p(x) = \frac{AE}{\beta R} \frac{e^{-x}}{x^2} h(x), \text{ with}$$

$$h(x) = p(x)x^2 e^x \tag{3}$$

The values of $p(x)$ and $h(x)$ are calculated *vs. x* by numerical integral and shown in Fig. 1. Compared with $p(x)$, $h(x)$ varies slowly and has an asymptotic value of 1 as x increases, and so it may be easier to explore reasonable approximations for $h(x)$.

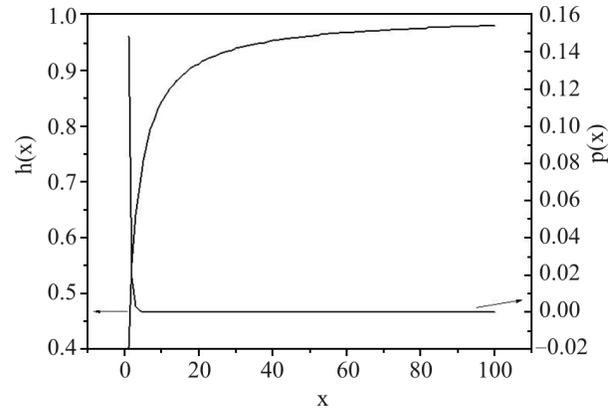The logarithmic form of Eq. (3) is adopted in almost all the integral methods for convenience of analysis:

Fig. 1 Values of $h(x)$ and $p(x)$ in the domain of $1{\leq}x{\leq}100$

$$\ln G(\alpha) = \ln\left[\frac{AE}{\beta R}\right] + \ln[p(x)] =$$

$$\ln\left[\frac{AE}{\beta R}\right] + \ln[h(x)] - 2\ln x - x \tag{4}$$

Various integral methods differ from each other just in their different ways to deal with the term of $\ln[h(x)]$. In terms of the different ways the integral methods fall into two types as follows.

Type A: Merging the term of ln[h(x)] into $\ln\left[\frac{AE}{\beta R}\right]$
[2–7]

This process leads to the expression:

$$\ln\frac{G(\alpha)}{T^2} = \ln\left[\frac{AR}{\beta E} h\left(\frac{E}{RT}\right)\right] - \frac{E}{RT} \tag{5}$$

This type assumes that the term of $\ln\left[\frac{AR}{\beta E} h\left(\frac{E}{RT}\right)\right]$ can be regarded as a constant for T, and thus the plot of $\ln\frac{G(\alpha)}{T^2}$ *vs.* the reciprocal of T would result in a straight line for a correct reaction model function. The activation energy E is obtained from the slope term of the regression line, and then the frequency factor A can be evaluated from the intercept term. For the methods of this type, the differences among them lie in the involved different approximations of temperature integral:

$$\ln\frac{G(\alpha)}{T^2} = \ln\left[\frac{AR}{\beta E}\left(1 - 2\frac{RT}{E}\right)\right] - \frac{E}{RT} \tag{6–1}$$

(Coats-Redfern's method [2])