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New approximate formula for Arrhenius temperature integral

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Abstract

In this paper a more precise approximate formula for Arrhenius temperature integral, i.e., $-\ln P(u) = 0.37773896 + 1.89466100 \ln u + 1.00145033u$, is proposed, by using two-step linearly fitting process: (i) the linear dependence of $\mathrm{d} \ln p(u)/\mathrm{d}u$ on $1/u$ and (ii) the linear dependence of $(\ln p(u) - c \ln u)$ on u. Values of $p(u)$ at different u were directly obtained from numerical integration of temperature integral without derivation from any approximating infinite series, and values of $\mathrm{d} \ln p(u)/\mathrm{d}u$ were obtained by numerical differentiating. New equation for the evaluation of non-isothermal kinetic parameters has been obtained from the above dependence, which can be put in the form

$$\ln\left[\frac{g(\alpha)}{T^{1.89466100}}\right] = \left[\ln\frac{AE}{\beta R} + 3.63504095 - 1.89466100 \ln E\right] - 1.00145033\frac{E}{RT}$$

The validity of this formula was confirmed and its deviation from the values of numerical integrating was discussed. Compared with some previously published approximate formulae, our formula has the best result in the kinetics analysis of non-isothermal process.

Keywords: Temperature integral; TGA; Non-isothermal kinetic analysis

1. Introduction

Last century had witnessed an accelerating use of thermal analysis techniques to investigate the kinetics of various isothermal and non-isothermal decompositions. Thermogravimetry (TG) may be one of the most popular thermal analysis techniques. And the reaction is carried out under a linear temperature program in the most of reported TG studies. An understanding of kinetic parameters, such as kinetic model, activation energy and the frequency factor, can be obtained by various approaches. The integral approach is generally believed to be more convenient, reliable, and accurate than the differential method [1]. It is usually assumed that the basic kinetic equation for solid-state decomposition process under non-isothermal conditions can be expressed as a function of the fractional conversion α $(0 < \alpha < 1)$ in the following form:

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

where A is the pre-exponential factor of the Arrhenius rate constant, E the apparent activation energy, β the heating rate, T the absolute temperature, R the gas constant, $f(\alpha)$ the reaction kinetics function.

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Rearranging Eq. (1) and integrating both sides of the equation, the following expression is obtained:

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^{T}\mathrm{e}^{-E/RT}\,\mathrm{d}T=\frac{AE}{\beta R}p(u),$$

$$p(u)=\int_{\infty}^{\alpha}\frac{-\mathrm{e}^{-u}}{u^2}\,\mathrm{d}u \qquad (2)$$

where $p(u)$ is the Arrhenius temperature integral, $u=E/RT$. Unfortunately, the right side of Eq. (2) cannot be analytically integrated. Consequently, extensive efforts have been devoted to obtain better integral approximations. In a recent paper, Flynn [2] has reviewed various evaluations and approximations for the temperature integral and reappraised their accuracies and utilities to evaluate the temperature integral in thermal analysis kinetics.

In 1986, Madhusudanan et al. [3] proposed an approximate formula for temperature integrating calculation, which can be readily rearranged for using in the field of iso-conversional method. Because of its simplicity the formula is commonly used in integral methods of thermal analysis [4–8]. This formula is shown below:

$$-\ln P(u)=0.297580+1.921503\ln u+1.000953u \qquad (3)$$

Two other equations [9] in the form of Eq. (3) were proposed for the evaluation of kinetic parameters from non-isothermal experiments later. These two equations reported are shown below:

$$-\ln P(u)=0.299963+1.920620\ln u+1.000974u \qquad (4)$$

$$-\ln P(u)=0.389677+1.884318\ln u+1.001928u \qquad (5)$$

Just as Heal [10] said, ‘Those early mathematical tables are themselves derived from some approximating infinite series, because there is, of course, no true value for the integral’. The question is not only “How precisely do the recent approximation fit the older standard tabulated data”, but also, “How reliable are the old data sets”. And he also pointed out that the tables used in the past, considering the date of publication, must have been produced without the aid of computers, and might contain errors. So he concluded that a new set of values, computer-calculated, were needed. When we reevaluated these literatures, we found that there was something to be improved.

In the literature [2], the authors declared that their approximate formula (Eq. (3)), which is called as MKN equation, was derived based on a two-term approximate formula, i.e. $(\mathrm{e}^{-u}/u^2)[(u+1)/(u+3)]$, which is just but an approximation of Eq. (2). That is, their approximate formula (Eq. (3)) was not directly derived from the original numerical values of temperature integral. Using the same method, in another literature [8], Eqs. (4) and (5) were derived based on the three-term approximate equation, i.e.

$$\frac{\mathrm{e}^{-u}}{u^2}\left[1-\frac{2}{u+3}-\frac{5}{(u+1)(u+2)(u+3)}\right]$$

and the series approximate equation for Arrhenius temperature integral, i.e.

$$\frac{\mathrm{e}^{-u}}{u^2}\left[1-\frac{2}{u+3}-\frac{6}{(u+1)\cdots(u+3)}\right.$$
$$\div\frac{28}{(u\div 1)\cdots(u+4)}-\frac{120}{(u+1)\cdots(u+5)}$$
$$\left.+\frac{496}{(u+1)\cdots(u+6)}-\cdots\right]$$

respectively. Taking into account the generalized use of MKN equation for temperature integral, it seems to be of great interest to check the accuracy of these approximations.

As we know, the values of temperature integral at different temperature interval can be easily obtained by numerical integral on a PC computer nowadays. If an approximate formula is directly derived, its accuracy and reliability will be higher than that derived indirectly. Furthermore, in order to delete the ambiguity accompanied by the interpretation of kinetic data produced from thermal analysis measurements, it is important to use adequate computational methods and experimental conditions. With accurate measurements of temperature, the use of proper approximate formula for the temperature integral allow us to calculate kinetic parameters as precisely as possible [2]. So we think it is necessary to reevaluate these approximations and to derive a more precise approximate formula. The main objective of this study is to present a precise integral approximate formula for kinetic analysis of non-isothermal thermogravimetric analysis (TGA) data. Because of its simplicity in calculation, the form will be remained and its accuracy will be enhanced in the newly proposed approximate formula.

2. Theoretical considerations and calculation procedure

As shown in Eqs. (3)–(5), it is assumed that the logarithm of temperature integral varies with u, which obeys the equation below, and can be put in the form:

$$\ln p(u) = a + bu + c \ln u \tag{6}$$

where $p(u)$ is so-called "temperature integral", $u = E/RT$, T the absolute temperature, E the activation energy, R the gas constant, and a, b, and c are the coefficients independent of u.

Differentiating both sides of Eq. (6), we obtain

$$\frac{\partial \ln p(u)}{\partial u} = b + \frac{c}{u} \tag{7}$$

Plotting $\partial \ln p(u)/\partial u$, i.e. $\mathrm{d}\ln p(u)/\mathrm{d}u$, versus $1/u$, we get a straight line. The slope of the line is c, while the intercept is b. Rearranging Eq. (6) and inserting the value of c, we obtain

$$\ln p(u) - c \ln u = a + bu \tag{8}$$

Plotting $(\ln p(u) - c \ln u)$ versus u, we get another straight line. The slope of the line is b, intercept is a. The value of intercept in Eq. (7) should be equal to that of slope in Eq. (8). Then we get all the coefficients of Eq. (6).

3. Results and discussion

The 'exact' value of the Arrhenius integral used for the error calculation was obtained by double precision numerical integration of temperature integral using the Simpson's procedure with a step size of 1 for u on a PC computer. And values of $\partial \ln p(u)/\partial u$ were obtained from cubic spline numerical differentiating. Since most of u encountered in experimental studies lies in the domain of $20 \le u \le 60$, different values of $P(u)$ at corresponding u were gained. The plots of Eqs. (7) and (8) are shown in Figs. 1 and 2, respectively.

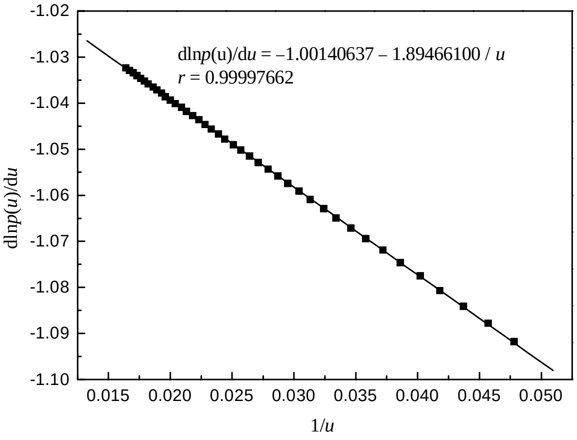

Fig. 1. Linear plotting of $\mathrm{d}\ln p(u)/\mathrm{d}u$ versus $1/u$.

From the linear plot of $\mathrm{d}\ln p(u)/\mathrm{d}u$ versus $1/u$, b, c, and linear regression coefficients were calculated and their values are as follows: $b = -1.00140637$, $c = -1.89466100$, $r = 0.99997662$. The values of a, b and coefficient, r, for the linear plot of $(\ln p(u) - c \ln u)$ versus u are: $a = -0.3773896$, $b = -1.00145033$, $r = 1.00000000$. The value of b obtained from Eq. (7) is quite close to that from Eq. (8), which validates Eq. (6) in the range $20 \le u \le 60$. The two values of b from Eqs. (7) and (8) and their mean value were also compared. The result showed that the value of b from Eq. (8) results in the highest accuracy.

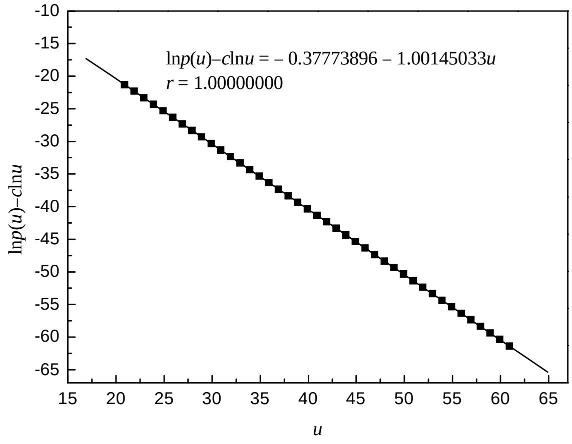

Fig. 2. Linear plotting of $\ln p(u) - c \ln u$ versus u.

When values of coefficients a, b, and c are obtained from Figs. 1 and 2, they are inserted into Eq. (6). A new form of approximation is shown as below:

$$-\ln P(u) = 0.37773896 + 1.89466100 \ln u + 1.00145033u \qquad (9)$$

Inserting Eq. (9) into Eq. (2), and logarithm on both sides of Eq. (2), we get

$$\ln\left[\frac{g(\alpha)}{T^{1.89466100}}\right] = \left[\ln\frac{AE}{\beta R} + 3.63504095 - 1.89466100 \ln E\right] - 1.00145033\frac{E}{RT} \qquad (10)$$

Plotting $\ln[g(\alpha)/T^{1.89466100}]$ versus $1/T$, the activation energy E is obtained from the slope and the pre-exponential factor A can be calculated by inserting E and heating rate β into the interception,

$$\left[\ln\frac{AE}{\beta R} + 3.63504095 - 1.89466100 \ln E\right]$$

Eqs. (3)–(5), and Eq. (9) have the same forms, but their coefficients are different, respectively. Doyle formula [11], one of the most widely used approximate formulae for $P(u)$, is also introduced for comparison

$$-\ln P(u) = 5.3308 + 1.0516u \qquad (11)$$

Table 1
Relative percent error for some approximate formula at various u

u	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (9)	Eq. (11)
5	13.4107	13.2898	9.2803	9.0243	−87.3576
10	4.4600	4.4016	2.7839	2.0515	−65.7565
15	1.9745	1.9433	1.3698	0.4634	−43.4410
20	1.0043	0.9885	0.9942	0.0299	−24.4140
25	0.5669	0.5604	0.9041	−0.0538	−10.3003
30	0.3509	0.3500	0.8818	−0.0281	−1.3662
35	0.2329	0.2351	0.8522	0.0194	2.8430
40	0.1571	0.1606	0.7875	0.0535	3.1096
45	0.0961	0.0995	0.6787	0.0601	0.3103
50	0.0359	0.0381	0.5244	0.0340	−4.7140
55	−0.0309	−0.0308	0.3262	−0.0256	−11.2238
60	−0.1081	−0.1108	0.0870	−0.1179	−18.6058
65	−0.1974	−0.2035	−0.1897	−0.2410	−26.3756
70	−0.2997	−0.3097	−0.5005	−0.3927	−34.1674

The relative percent errors associated with the use of MKN approximate formulae, Doyle formula, and Eq. (9) as solution of the Arrhenius integral for various u are shown in Table 1, respectively. The relative percent errors associated with the use of these approximate formulae as solution of the Arrhenius integral for a physically realistic domain of u are plotted in Fig. 3. The line (–■–) represents the values of temperature integral at different u ($5 \leq u \leq 70$) calculated by using numerical integral method with Simpson's rule. Meanwhile, the other lines represent the values calculated by using Eqs. (3)–(5), (9) and (11), respectively. Fig. 3 shows that Eq. (9) is significantly more accurate than either of Eqs. (3)–(5) or (11), as a solution of Arrhenius integral. As shown in Fig. 3. The precisions of Eqs. (5) and (11) are rough and the range of their applicability is narrow. Eqs. (3) and (4) almost have the same precision at different values of u, for their plots are nearly superposed with each other. Eq. (9) is better than both Eqs. (3) and (4) almost in all the range of u. The typical deviation of these five kinds of equations from 'exact' values of $p(u)$ at different u is shown in Table 2. Eq. (9) under-predicts the true value of the Arrhenius integral by less than 1% over the domain $u \geq 13$, which is often encountered in experimental studies. From Fig. 3 we can see that Eq. (9) is much superior to Eqs. (3)–(5). And we also investigated other possible approximations in the form of Eq. (6), in which Eq. (9) is best. Fur-

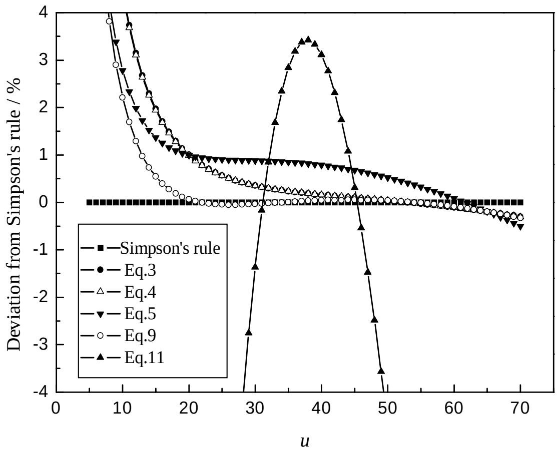

Fig. 3. Comparison of various approximate methods at different values of u.

Table 2
The range of their use for some temperature integral approximate formulae and their relative percent error

Approximate equation	Range of u				
	Deviation from Simpson's rule (%)				
	<0.1	<0.5	<1.0	<2.0	<5.0
Eq. (3)	$45 \le u \le 59$	≥ 27	≥ 20	≥ 15	≥ 10
Eq. (4)	$45 \le u \le 59$	≥ 27	≥ 20	≥ 15	≥ 10
Eq. (5)	$60 \le u \le 63$	$51 \le u \le 70$	≥ 20	≥ 12	≥ 8
Eq. (9)	$19 \le u \le 59$	≥ 15	≥ 13	≥ 11	≥ 7
Eq. (11)	–	–	–	–	$28 \le u \le 50$

thermore, Eq. (9) is directly derived from numerical temperature integral without derivation from any approximating infinite series, so it is reliable. So we are sure that Eq. (9) is an ideal choice in the treatment of TGA data.

All calculation mentioned above was run by a program compiled in MATLAB 5.3 language, which is a powerful soft ware for numerical calculation and symbol calculation. The precision of numerical calculation performed is higher than $\pm 10^{-11}\%$ [12].

4. Conclusions

The accuracy and reliability of three MKN approximate formulae, which have the form, $-\ln p(u) = a + bu + c\ln u$, are reevaluated by the numerical analysis. A improved approximation for temperature integral, $-\ln P(u) = 0.37773896 + 1.89466100\ln u + 1.00145033u$, has been proposed by using two-step linear fitting process. High linearly fitting coefficients and sameness of b from Eqs. (7) and (8) confirm the validity of this newly proposed equation. The results show that this modified approximation has higher accuracy and reliability than that ever published, and is an ideal choice for temperature integral.

Acknowledgements

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References

[1] J.H. Flynn, L.A. Wall, J. Res. NBS A 70 (1966) 209.
[2] J.H. Flynn, Thermochim. Acta 300 (1997) 83.
[3] P.M. Madhusudanan, K. Krishnan, K.N. Ninan, Thermochim. Acta 97 (1986) 189.
[4] El-H.M. Diefallah, M.A. Gabal, A.A. El-Bellihi, N.A. Eissa, Thermochim. Acta 376 (2001) 43.
[5] S.A. Antony, C. Mallika, V. Sridharan, K.S. Nagaraja, O.M. Sreedharan, Thermochim. Acta 378 (2001) 125.
[6] A.Y. Obaid, A.O. Alyoubi, A.A. Samarkandy, S.A. Al-Thabaiti, S.S. Al-Juaid, A.A. El-Bellihi, El-H.M. Deifallah, J. Therm. Anal. Cal. 61 (2000) 985.
[7] G. Singh, I.P.S. Kapoor, J. Kaur, Thermochim. Acta 351 (2000) 139.
[8] J.J.M. Orfao, F.G. Martuns, Themochim. Acta 390 (2002) 195.
[9] P.M. Madhusudanan, K. Krishnan, K.N. Ninan, Thermochim. Acta 221 (1993) 13.
[10] G.R. Heal, Thermochim. Acta 340/341 (1999) 69.
[11] C.D. Doyle, J. Apl. Polym. Sci. 6 (24) (1962) 639.
[12] E. Urbanovici, C. Popescu, E. Segal, J. Therm. Anal. Cal. 55 (1) (1999) 325.