Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 3, 885–889

NEW RATIONAL FRACTION APPROXIMATING FORMULAS FOR THE TEMPERATURE INTEGRAL

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Three rational fraction approximations for the temperature integral have been proposed using the pattern search method. The validity of the new approximations has been tested by some numerical analyses. Compared with several published approximating formulas, the new approximations is more accurate than all approximations except the approximations proposed by Senum and Yang in the range of $5\leq E/RT\leq 100$. For low values of E/RT, the new approximations are superior to Senum-Yang approximations as solutions of the temperature integral.

Keywords: *approximation, kinetic parameters, non-isothermal kinetics, temperature integral*

Introduction

Thermogravimetric analysis (TG), especially nonisothermal TG, provides a quantitative understanding the kinetics of processes involving solids, such as decomposition and gas-solid reactions, by following the mass loss and/or the rate of mass loss of the samples with time [1]. Knowledge of the kinetic parameters, such as the activation energy and the frequency factor, can be obtained through various TG data treating methods. Since their many inherent advantages, integral methods have been widely used to determine kinetic parameters from nonisothermal TG data [2]. Unfortunately, integral methods involves the integral of the Arrhenius function, so called 'temperature integral', which does not have an exact analytical solution. A large number of approximate solutions for the temperature integral, with varying complexity and precision, have been proposed [3]. Overviews of the temperature integral approximations and their applications can be found in the literature [4–6]. However, some approximations are imprecise in the evaluation of the temperature integral if the approximations are compared with the values calculated by numerical integration [7]. Junmeng *et al*. have developed two new first degree rational fraction approximations for the temperature integral, which is simple and accurate [8, 9]. The present work seeks to develop several more accurate approximations for the temperature integral under experimental conditions of a linear temperature program and extend these results to the unambiguous determination of the kinetic parameters. It is hoped that the results of this work will aid process development of nonisothermal kinetics.

Theoretical

The temperature integral is a special integral which frequently occurs in the non-isothermal kinetic analysis when the dependence of the reaction rate on the temperature is described by the Arrhenius law [10]. The expression of the temperature integral is $\int_0^T e^{-E/RT}dT$, where T is the absolute temperature, E is the activation energy, R is the universal gas constant. If E/RT is replaced by 'u' and the integration limits are transformed, the temperature integral becomes

$$\int_0^T e^{-E/RT}dT=\frac{E}{R}P(u)=\frac{E}{R}\int_u^{\infty}\frac{e^{-u}}{u^2}du \tag{1}$$

where $P(u)$ is the exponential integral.

The $P(u)$ function does not have an exact analytical solution, but can be numerically integrated. In this study, we use the following second and third degree rational fraction to approximate the $P(u)$ function.

$$P_1(u)=\frac{e^{-u}}{u^2}\frac{u^2+p_1u+p_2}{u^2+p_3u+p_4} \tag{2}$$

$$P_2(u)=\frac{e^{-u}}{u^2}\frac{u^2+p_5u+p_6\ln u+p_7}{u^2+p_8u+p_9\ln u+p_{10}} \tag{3}$$

$$P_3(u)=\frac{e^{-u}}{u^2}\frac{u^3+p_{11}u^2+p_{12}u+p_{13}}{u^3+p_{14}u^2+p_{15}u+p_{16}} \tag{4}$$

where p_1–p_{16} are indeterminant parameters. Here we call the above expressions Ji approximation I, Ji approximation II and Ji approximation III.

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1388–6150/$20.00

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Most solid-state reactions take place in the range of $5 \le u \le 100$. To determine the values of p_1–p_{16}, the following objective function is established:

$$O.F. = \int_{5}^{100} [p(u) - p_i(u)]^2 \mathrm{d}u, \quad i=1, 2, 3 \qquad (5)$$

Those values which minimize the objective function are the expected values. It is difficult to get the derivative information of the objective function which does not have explicit expression. The optimization algorithm should be derivative-free, robust with respect to local optima. In this work, we have employed the pattern search to solve the above optimization problem. The pattern search method is a derivative-free, direct search algorithm for nonlinear optimization. Detailed information of the pattern search method can be found in the literature [8, 11, 12]. Thus, the approximations for the $P(u)$ function are obtained and given below:

$$P_1(u) = \frac{e^{-u}}{u^2} \frac{u^2 + 4.45239u + 0.76927}{u^2 + 6.45218u + 7.69430} \qquad (6)$$

$$P_2(u) = \frac{e^{-u}}{u^2} \frac{u^2 + 16.99864u + 3.65517\ln u + 5.41337}{u^2 + 18.99977u + 3.43593\ln u + 38.49858} \qquad (7)$$

$$P_3(u) = \frac{e^{-u}}{u^2} \frac{u^3 + 9.27052u^2 + 16.79440u + 1.20025}{u^3 + 11.27052u^2 + 33.33602u + 24.21457} \qquad (8)$$

From Eqs (1), (6), (7) and (8), the corresponding approximations for the temperature integral are obtained:

Table 1 Expressions of the approximation for the exponential integral

Author		$P(u)$	Equation
Coats and Redfern [13]		$\frac{e^{-u}}{u^2}\left(1-\frac{2}{u}\right)$	(12)
Gorbachev [14]		$\frac{e^{-u}}{u}\frac{1}{u+2}$	(13)
Chung-Hsiung [15]		$\frac{e^{-u}}{u^2}\frac{1-(2/u)}{1-(6/u^2)}$	(14)
Agrawal [16]		$\frac{e^{-u}}{u^2}\frac{1-(2/u)}{1-(5/u^2)}$	(15)
Quanyin and Su [17]		$\frac{e^{-u}}{u^2}\frac{1-(2/u)}{1-(4.6/u^2)}$	(16)
Wanjun *et al.* [18]		$\frac{e^{-u}}{u}\frac{1}{1.00198882u+1.87391198}$	(17)
Senum and Yang [19]	Second degree	$\frac{e^{-u}}{u}\frac{u+4}{u^2+6u+6}$	(18)
	Third degree	$\frac{e^{-u}}{u}\frac{u^2+10u+18}{u^3+12u^2+36u+24}$	(19)
	Fourth degree	$\frac{e^{-u}}{u}\frac{u^3+18u^2+86u+96}{u^4+20u^3+120u^2+240u+120}$	(20)
Junmeng *et al.* [8]		$\frac{e^{-u}}{u^2}\frac{u+0.66691}{u+2.64943}$	(21)
Junmeng and Fang [9]		$\frac{e^{-u}}{u^2}\frac{0.99962u+0.60462}{u+2.56879}$	(22)
Ji	Approximation I	$P_1(u)=\frac{e^{-u}}{u^2}\frac{u^2+4.45239u+0.76927}{u^2+6.45218u+7.69430}$	(6)
	Approximation II	$P_2(u)=\frac{e^{-u}}{u^2}\frac{u^2+16.99864u+3.65517\ln u+5.41337}{u^2+18.99977u+3.43593\ln u+38.49858}$	(7)
	Approximation III	$P_3(u)=\frac{e^{-u}}{u^2}\frac{u^3+9.27052u^2+16.79440u+1.20025}{u^3+11.27052u^2+33.33602u+24.21457}$	(8)

Table 2 Relative error percentages of the $P(u)$ approximations for the estimation of the $P(u)$ function

u	Coats and Redfern	Gorbachev	Chung-Hsiung	Agrawal	Quanyin and Su	Wanjun *et al.*	Senum and Yang 2nd degree	Senum and Yang 3rd degree	Senum and Yang 4th degree	Junmeng *et al.*	Junmeng and Fang	Ji I	Ji II	Ji III
5	–1.8858E+01	–3.4025E+00	6.7656E+00	1.4273E+00	–5.6143E-01	–1.7727E+00	–2.3540E-01	–2.3925E-02	–3.1323E-03	1.8692E-01	9.4321E-02	8.0667E-04	9.1589E-06	4.0775E-06
10	–5.1758E+00	–1.2248E+00	8.7679E-01	–1.8507E-01	–6.0358E-01	–3.4284E-01	–3.4743E-02	–1.5830E-03	–9.9308E-05	–4.6774E-02	–3.6622E-02	1.3824E-04	7.6444E-06	–3.3609E-07
15	–2.3955E+00	–6.2890E-01	2.7860E-01	–1.7722E-01	–3.5838E-01	–6.3049E-02	–9.7680E-03	–2.5575E-04	–9.5774E-06	–2.9834E-02	–1.2443E-02	8.1231E-05	1.4019E-05	–2.4363E-07
20	–1.3787E+00	–3.8253E-01	1.2314E-01	–1.3033E-01	–2.3136E-01	9.8349E-03	–3.7556E-03	–6.4086E-05	–1.6039E-06	–1.2326E-02	1.2114E-03	–3.4246E-05	–9.3308E-06	4.5297E-07
25	–8.9552E-01	–2.5716E-01	6.5106E-02	–9.6289E-02	–1.6070E-01	2.5751E-02	–1.7415E-03	–2.0938E-05	–3.7587E-07	–1.6420E-03	6.7545E-03	–7.6376E-05	–1.6648E-05	3.9241E-07
30	–6.2836E-01	–1.8474E-01	3.8563E-02	–7.3212E-02	–1.1785E-01	2.2883E-02	–9.1538E-04	–8.1789E-06	–1.1060E-07	4.6267E-03	8.2995E-03	–7.8557E-05	–1.2338E-05	1.2098E-07
35	–4.6520E-01	–1.3913E-01	2.4715E-02	–5.7273E-02	–9.0030E-02	1.3542E-02	–5.2639E-04	–3.6346E-06	–3.8381E-08	8.3181E-03	7.9412E-03	–6.4871E-05	–4.2746E-06	–1.0747E-07
40	–3.5828E-01	–1.0855E-01	1.6786E-02	–4.5921E-02	–7.0981E-02	2.2520E-03	–3.2391E-04	–1.7806E-06	–1.5097E-08	1.0492E-02	6.6920E-03	–4.6539E-05	3.3075E-06	–2.4084E-07
45	–2.8441E-01	–8.7053E-02	1.1920E-02	–3.7591E-02	–5.7382E-02	–9.2069E-03	–2.1013E-04	–9.4166E-07	–6.5525E-09	1.1751E-02	5.0511E-03	–2.8245E-05	8.7957E-06	–2.9179E-07
50	–2.3125E-01	–7.1367E-02	8.7680E-03	–3.1316E-02	–4.7340E-02	–2.0133E-02	–1.4223E-04	–5.2960E-07	–3.0788E-09	1.2442E-02	3.2703E-03	–1.1743E-05	1.1879E-05	–2.8506E-07
55	–1.9172E-01	–5.9570E-02	6.6373E-03	–2.6477E-02	–3.9717E-02	–3.0276E-02	–9.9683E-05	–3.1333E-07	–1.5445E-09	1.2775E-02	1.4777E-03	2.4765E-06	1.2786E-05	–2.4222E-07
60	–1.6153E-01	–5.0475E-02	5.1451E-03	–2.2673E-02	–3.3796E-02	–3.9578E-02	–7.1927E-05	–1.9341E-07	–8.2125E-10	1.2878E-02	–2.6216E-04	1.4444E-05	1.1919E-05	–1.7897E-07
65	–1.3795E-01	–4.3315E-02	4.0689E-03	–1.9629E-02	–2.9105E-02	–4.8067E-02	–5.3196E-05	–1.2377E-07	–4.5749E-10	1.2833E-02	–1.9186E-03	2.4386E-05	9.6954E-06	–1.0582E-07
70	–1.1918E-01	–3.7578E-02	3.2733E-03	–1.7156E-02	–2.5326E-02	–5.5803E-02	–4.0187E-05	–8.1698E-08	–2.6173E-10	1.2692E-02	–3.4787E-03	3.2578E-05	6.4818E-06	–2.9543E-08
75	–1.0400E-01	–3.2909E-02	2.6724E-03	–1.5122E-02	–2.2238E-02	–6.2856E-02	–3.0923E-05	–5.5406E-08	–1.5996E-10	1.2490E-02	–4.9397E-03	3.9294E-05	2.5810E-06	4.5716E-08
80	–9.1542E-02	–2.9060E-02	2.2101E-03	–1.3428E-02	–1.9681E-02	–6.9298E-02	–2.4182E-05	–3.8476E-08	–1.0098E-10	1.2250E-02	–6.3036E-03	4.4775E-05	–1.7678E-06	1.1753E-07
85	–8.1198E-02	–2.5849E-02	1.8485E-03	–1.2002E-02	–1.7541E-02	–7.5193E-02	–1.9182E-05	–2.7281E-08	–6.2517E-11	1.1987E-02	–7.5753E-03	4.9229E-05	–6.3803E-06	1.8459E-07
90	–7.2513E-02	–2.3142E-02	1.5618E-03	–1.0792E-02	–1.5732E-02	–8.0602E-02	–1.5410E-05	–1.9710E-08	–4.1425E-11	1.1713E-02	–8.7606E-03	5.2831E-05	–1.1117E-05	2.4628E-07
95	–6.5151E-02	–2.0839E-02	1.3314E-03	–9.7552E-03	–1.4189E-02	–8.5578E-02	–1.2522E-05	–1.4478E-08	–2.5297E-11	1.1433E-02	–9.8661E-03	5.5726E-05	–1.5875E-05	3.0244E-07
100	–5.8856E-02	–1.8864E-02	1.1443E-03	–8.8609E-03	–1.2862E-02	–9.0166E-02	–1.0280E-05	–1.0799E-08	–1.8070E-11	1.1153E-02	–1.0898E-02	5.8035E-05	–2.0579E-05	3.5315E-07

$$\int_0^T e^{-E/RT}dT = \frac{RT^2}{E}\frac{(E/RT)^2+4.45239(E/RT)+0.76927}{(E/RT)^2+6.45218(E/RT)+7.69430}e^{-E/RT} \quad (6)$$

$$\int_0^T e^{-E/RT}dT = \frac{RT^2}{E}\frac{(E/RT)^2+16.99864(E/RT)+3.65517\ln(E/RT)+5.41337}{(E/RT)^2+18.99977(E/RT)+3.43593\ln(E/RT)+38.49858}e^{-E/RT} \quad (7)$$

$$\int_0^T e^{-E/RT}dT = \frac{RT^2}{E}\frac{(E/RT)^3+9.27052(E/RT)^2+16.79440(E/RT)+1.20025}{(E/RT)^3+11.27052(E/RT)^2+33.33602(E/RT)+24.21457}e^{-E/RT} \quad (8)$$

Table 3 The range of u in which the new approximations are accurate than Senum–Yang approximations

	Senum–Yang second degree approximation	Senum–Yang third degree approximation	Senum–Yang fourth degree approximation
Ji approximation I	$5\le u\le 72$	$5\le u\le 21$	$5\le u\le 9$
Ji approximation II	$5\le u\le 92$	$5\le u\le 26$	$5\le u\le 18$
Ji approximation III	$5\le u\le 100$	$5\le u\le 75$	$5\le u\le 24$

Accuracy evaluation of the approximations

Since the exponential integral is the variable-transformed expression of the temperature integral, the accuracy evaluation of the temperature integral approximation is identical to that of the corresponding exponential integral approximation. Most thermally stimulated solid-state reactions take place in the range of $5\le u\le 100$. Here we consider this range of u in the following accuracy evaluation.

Here we introduced some existed approximations proposed by Coats and Redfern [13], Gorbachev [14], Chung-Hsiung [15], Agrawal [16], Quanyin and Su [17], Wanjun *et al.* [18]. Senum and Yang [19], Junmeng *et al.*. [8] and Junmeng and Fang [9] for comparison. The expressions of those approximations are listed in Table 1.

The relative error percentages of those approximations for the estimation of $P(u)$ are illustrated in Table 2. The relative error has been defined by the following expression:

$$\varepsilon = \frac{P_a(u) - P(u)}{P(u)} \cdot 100\% \quad (23)$$

where $P_a(u)$ is the value obtained by the $P(u)$ approximation, and $P(u)$ is the value obtained by numerical integration which is performed by means of the Mathematica software system.

From the obtained relative errors included in Table 2, we can obtain that the three newly proposed approximations are more accurate than those approximations proposed by Coats and Redfern, Gorbachev, Chung-Hsiung, Agrawal, Quanyin and Su, Wanjun *et al.*, Junmeng *et al.* and Junmeng and Fang in the range of $5\le u\le 100$. In general, the three approximations are accurate than Senum–Yang approximations for low values of u. The ranges of u in which the new approximations are accurate than Senum–Yang approximations are listed in Table 3. Furthermore, the absolute value of the relative error of the three new approximations for the estimation of the temperature integral are less than $8.1\cdot 10^{-4}$, $2.5\cdot 10^{-5}$, $4.1\cdot 10^{-6}$% in the range of $5\le u\le 100$, respectively. Therefore, the three newly proposed approximations are accurate and can be used for performing the non-isothermal kinetic analysis of solid-state reactions.

Conclusions

Three new rational fraction approximations for the temperature integral have been obtained using the pattern search method. The relative errors of the new approximations for the estimation of the temperature integral are obtained and very low. Compared with several temperature integral approximations, the newly proposed approximations give more accurate values of the temperature integral than some other approximating formulas except Senum–Yang approximations in the range of $5\le E/RT\le 100$. For low values of E/RT, the new approximations are accurate than Senum–Yang approximations as solutions of the temperature integral.

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Received: March 4, 2007
Accepted: March 5, 2007

DOI: 10.1007/s10973-007-8279-1