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CALCULATION OF THE INTEGRAL $\int_0^T T'^m \exp(-E/RT')\mathrm{d}T'$

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Abstract

A technique has been developed for the calculation of the

$$\int_0^T T'^m \exp(-E/RT')\mathrm{d}T'.$$

The accuracy of the method is tested by comparing its predictions with numerical results and those of a method due to Quanyin and Su.

Keywords: non-isothermal processes, temperature exponent

Introduction

Techniques based on non-isothermal thermoanalytical methods such as differential thermal analysis (DTA), thermogravimetry (TG) etc. [1, 2] find wide applications in the analysis of variety of reactions. A serious difficulty of the mathematical modelling of the non-isothermal processes results from the fact that the integral

$$\int_0^T T'^m \exp(-E/RT')\mathrm{d}T'$$

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(E, activation energy, R, universal gas constant, T, absolute temperature) can not be solved in a closed form. The exponent m arises from the temperature dependence of the pre-exponential factor. The cases m=1/2 and m=1 occur respectively in the collision theory and transition state theory [3–5]. The first case describes a surface reaction between a gaseous and solid reactant and second one represents single reactant solid state decomposition. However, other possibilities do exist to describe such reactions as solid–solid diffusion controlled and pressure-dependent reactions.

Recently Quanyin and Su [6] proposed new approximations for the evaluation of the integral

$$\int_0^T T'^{m} \exp(-E/RT')\mathrm{d}T'$$

for the special case of m=0. In the present paper we consider evaluation of the integral for arbitrary values of the temperature exponent m. The suitability of the present technique is assessed by comparing its prediction with that of the numerical evaluation using Gauss-Legendre quadrature [7].

Theory

Let

$$I(m,T)=\int_0^T T'^{m} \exp\left(-\frac{E}{RT'}\right)\mathrm{d}T'. \tag{1}$$

With the substitution $t'=E/RT'$ Eq. (1) can be expressed as

$$I(m,T)=\left\{\frac{E}{R}\right\}^{(m+1)} \int_t^\infty \frac{\exp(-t')}{t'^{(m+2)}}\mathrm{d}t' \tag{2}$$

Let us use the integral representation [7]

$$\int_t^\infty \frac{\exp(-t')}{t'^{(-m+1)}}\mathrm{d}t'=\Gamma(m,t) \tag{3}$$

where $\Gamma(m,t)$ is the complementary incomplete gamma function [7].

Now, Eq. (2) can be expressed as

$$I(m,T)=\left\{\frac{E}{R}\right\}^{m+1} \Gamma(-m-1,t) \tag{4}$$

It is evident from Eq. (3) that in order to evaluate $I(m,T)$ one has to evaluate the complementary incomplete gamma function $\Gamma(m,t)$. We evaluate $\Gamma(m,t)$ by using a technique outlined by Sil [8]. Near $t=m$, $\Gamma(m,t)$ varies more rapidly. For $t<m+1$ it is evaluated by using its continued fraction representation [9] given by

$$\Gamma(m,t)=\cfrac{t_{m}e^{-t}}{x+\cfrac{1-m}{1+\cfrac{1}{x+\cfrac{2-m}{1+\cfrac{2}{x+\cfrac{3-m}{1+\ldots}}}}}} \tag{5}$$

The continued fraction is evaluated by the rigorous quotient-difference algorithm [10, 11]. The advantage of using the continued fraction representation is its rapid convergence and high accuracy. For $t>m+1$, $\Gamma(m,t)$ is evaluated by using a series expansion [7] given by

$$\Gamma(m,t)=1-\exp(-t)t^{m}\sum_{n=0}^{\infty}\frac{\Gamma(m)}{\Gamma(m+1+n)t^{n}} \tag{6}$$

$\Gamma(z)$ is the gamma function. It is evaluated by using the algorithm developed by Roy *et al*. [12].

Finally $I(m, T)$ is evaluated numerically by using Gauss-Legendre quadrature [7]. According to this method any integral

$$J=\int_{a}^{b} f(x)\mathrm{d}x$$

is first converted into another one with limits betwen –1 and +1 through the transformation [7] $x=0.5[(b-a)z+b+a]$ so that one can write

$$J=0.5(b-a)\int_{-1}^{+1} f[0.5\{(b-a)z+b+a\}]\mathrm{d}z \tag{7}$$

In the Gauss-Legendre quadrature method the definite integral in Eq. (7) is approximated by a properly weighted sum of any number of particular values v_j suitably distributed between –1 and +1. If we take n terms Eq. (7) becomes

$$J=0.5(b-a)\sum_{j=1}^{n} f[0.5(b-a)v_{j}+0.5(b+a)]g_{j} \tag{8}$$

where v_j's and g_j's ($j=1$, n) are, respectively, called Gauss-Legendre points and Gauss-Legendre weight factors. Values of v_j and g_j for different n values are listed in Abramowitz and Stegun [7].

For accurate numerical evaluation of $I(m,T)$ we have to partition the interval $(0, T)$ into a number of sub-intervals [8] enabling us to write

$$I(m,T)=\int_{0}^{T_1} T'^{m}\exp\left(-\frac{E}{RT'}\right)\mathrm{d}T'+\int_{T_1}^{T_2} T'^{m}\exp\left(-\frac{E}{RT'}\right)\mathrm{d}T'+\ldots+\int_{T_n}^{T} T'^{m}\exp\left(-\frac{E}{RT'}\right)\mathrm{d}T' \tag{9}$$

We take T_1=10 K, T_2=20 K... etc. For each sub-interval the integral

$$I(m,T)=\int_{T_i}^{T} T'^{m}\exp(-E/RT')\mathrm{d}T'$$

have been evaluated by using a 32 point Gauss-Legendre quadrature. By partitioning technique the effective number of Gaussian points is increased.

Results and discussion

In Table 1 we report the present values of $I(m,T)$ for m=0 together with the results of the numerical integration. We see from Table 1 that present results agree well with numerical results. In Table 1 we also present the values of $I(0,t)$ by using the approximation of Quanyin and Su [6]. We have used their expression of higher accuracy. It is evident from Table 1 that unlike the present method their results never completely agree with the numerical ones. Actually their method fails for t<5.0. Similarly it is evident from Tables 2 and 3 that the present method also work well for non-zero values of m.

Table 1 Values of $I(m,T)$ for m=0. $A(B)$ stands for $A\cdot10^{B}$

t	Present	Numerical	Quanyin and Su
1	1.4850(2)	1.4850(2)	1.3244(3)
2	3.7534(1)	3.7534(1)	0.0
3	1.0642(1)	1.0642(1)	2.7045(1)
4	3.1982(0)	3.1982(1)	1.6312(1)
5	9.9647(–1)	9.9647(–1)	6.5978(–1)
6	3.1826(–1)	3.1826(–1)	2.4022(–1)
7	1.0351(–1)	1.0351(–1)	8.4313(–1)
8	3.4138(–2)	3.4138(–2)	2.9189(–1)
9	1.1384(–2)	1.1384(–2)	1.0059(–2)
10	3.8302(–3)	3.8302(–3)	3.4649(–3)
15	1.8108(–5)	1.8108(–5)	1.7313(–5)
20	9.4048(–8)	9.4048(–8)	9.1685(–5)
25	5.1569(–10)	5.1569(–10)	5.0731(–10)
30	2.3437(–12)	2.3437(–12)	2.3171(–12)
40	6.0757(–17)	6.0757(–17)	6.0365(–17)
50	1.8559(–21)	1.8559(–21)	1.8482(–21)
60	5.6522(–26)	5.6522(–26)	5.6359(–26)
70	2.7618(–30)	2.7618(–30)	2.7559(–30)

Table 2 Values of $I(m,T)$ for m=0.5 and 1; $A(B)$ stands for $A \cdot 10^B$

t	$I(0.5,T)$		$I(1,T)$	
	Present	Numerical	Present	Numerical
1	4.0000(3)	4.0000(3)	1.0969(5)	1.0969(5)
2	1.0584(3)	1.0584(3)	3.0133(4)	3.0133(4)
3	3.0732(2)	3.0732(2)	8.9306(3)	8.9306(3)
4	9.3764(1)	9.3764(1)	2.7613(3)	2.7613(3)
5	2.9525(1)	2.9525(1)	8.7780(2)	8.7780(2)
6	9.5044(0)	9.5044(0)	2.8460(2)	2.8460(2)
7	3.1102(0)	3.1102(0)	9.3657(1)	9.3657(1)
8	1.0308(0)	1.0308(0)	3.1181(1)	3.1181(1)
9	3.4511(–1)	3.4511(–1)	1.0479(1)	1.0479(1)
10	1.1651(–1)	1.1651(–1)	3.5488(0)	3.5488(0)
15	5.5692(–4)	5.5692(–4)	1.7140(–2)	1.7140(–2)
20	2.9102(–6)	2.9102(–6)	9.0091(–5)	9.0091(–5)
25	1.6020(–8)	1.6020(–8)	4.9779(–7)	4.9779(–7)
30	6.5296(–11)	6.5296(–11)	1.8196(–9)	1.8196(–9)
40	1.4711(–15)	1.4711(–15)	3.5623(–14)	3.5623(–14)
50	4.1110(–20)	4.1110(–20)	9.1073(–19)	9.1073(–19)
60	1.5674(–24)	1.5674(–24)	3.4774(–23)	3.4774(–23)
70	6.1334(–29)	6.1334(–29)	1.3622(–27)	1.3622(–27)

Table 3 Values of $I(m,T)$ for m= –0.5 and m= –1; $A(B)$ stands for $A \cdot 10^B$

t	$I(-0.5,T)$		$I(-1,T)$	
	Present	Numerical	Present	Numerical
1	5.6335(0)	5.6335(0)	2.1938(–1)	2.1938(–1)
2	1.3460(0)	1.3460(0)	4.8900(–2)	4.8900(–2)
3	3.7114(–1)	3.7114(–1)	1.3048(–2)	1.3048(–2)
4	1.0964(–1)	1.0964(–1)	3.7794(–3)	3.7794(–3)
5	3.3757(–2)	3.3757(–2)	1.1483(–3)	1.1483(–3)
6	1.0688(–2)	1.0688(–2)	3.6008(–4)	3.6008(–4)
7	3.4530(–3)	3.4503(–3)	1.1548(–4)	1.1548(–4)
8	1.1328(–3)	1.1328(–3)	3.7666(–5)	3.7665(–5)
9	3.7610(–4)	3.7610(–4)	1.2447(–5)	1.2447(–5)
10	1.2609(–4)	1.2609(–4)	4.1570(–6)	4.1570(–6)
15	5.8921(–7)	5.8921(–7)	1.9186(–8)	1.9186(–8)
20	3.0407(–9)	3.0407(–9)	9.8355(–11)	9.8355(–11)

Table 3 Continued

t	$I(-0.5,T)$		$I(-1,T)$	
	Present	Numerical	Present	Numerical
25	1.6606(–11)	1.6606(–11)	5.3489(–13)	5.3489(–13)
30	8.4143(–14)	8.4143(–14)	3.0216(–15)	3.0216(–15)
40	2.5096(–18)	2.5096(–18)	1.0368(–19)	1.0368(–19)
50	8.3790(–23)	8.3790(–23)	3.7833(–24)	3.7833(–24)
60	3.1850(–27)	3.1850(–27)	1.4359(–28)	1.4359(–28)
70	1.2436(–31)	1.2436(–31)	5.6003(–33)	5.6003(–33)

Conclusions

In the present paper we have developed a method for the evaluation of the integral

$$\int_0^T T'^m \exp(-E/RT')\mathrm{d}T'$$

which frequently occurs in the problems of thermal analysis. The values of the integral calculated by the present method agree well with numerical results both for $m=0$ and $m\neq 0$ and $1\leq t\leq 70$ ($t=E/RT$). On the other hand the recent prescription of Quanyin and Su [6] for the evaluation of the integral can be applied only for $m=0$ and fails for $t<5.0$ and never completely agrees with the numerical results for other values of t.

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References

1 W. G. Devi, Proc. 8th Manipur Science Congress, Manipur University, Imphal 1997, p. 14.
2 R. Chen and Y. Kirsh, Analysis of Thermally Stimulated Processes, Pergamon Press, Oxford 1981.
3 P. K. Gallagher and D. W. Johnson Jr., Thermochim. Acta, 6 (1973) 67.
4 J. Zsako and H. E. Arz, J. Thermal Anal., 6 (1974) 651.
5 P. Vallet, Thermogravimetry, Gauthier-Villars, Paris 1972.
6 R. Quanyin and Y. Su, J. Thermal Anal., 44 (1995) 1147.
7 M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions, Dover Publ., New York 1965.
8 N. C. Sil, Private Communication, 1997.
9 A. Erdélyi, Higher Transcendental Functions, Vol. 2, McGraw-Hill, New York, Ch. 9, 1953.
10 C. T. Fike, Computer Evaluation of Mathematical Functions, Prentice Hall, New Jersey 1968.
11 S. F. Action, Numerical Methods, Harper and Row, New York, Ch. 11, 1970.
12 A. Roy, K. Roy and N. C. Sil, J. Phys. B., 13 (1980) 3443.