Thermochimica Acta, 189 (1991) 171–174
Elsevier Science Publishers B.V., Amsterdam

Note

On the evaluation of the temperature integral with special reference to thermal analysis

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(Received 22 January 1991)

We consider the evaluation of the temperature integral

$$I(T_1, T_2) = \int_{T_1}^{T_2} T^a \exp(-E/RT)\, \mathrm{d}T \tag{1}$$

which occurs in the kinetic analysis of the thermogravimetric data [1,2]. The case $a = 0$ has been considered by a number of workers [2–9]. The case $a \neq 0$ usually occurs when the pre-exponential factor of the Arrhenius equation is temperature dependent [10].

We can write $I(T_1, T_2)$ as

$$I(T_1, T_2) = J(T_2) - J(T_1) \tag{2}$$

with

$$J(T) = \int_0^T T'^a \exp(-E/RT')\, \mathrm{d}T' \tag{3}$$

For $A = -2$, eqn (3) can be evaluated exactly [11] and for $a < -2$, eqn. (3) can be reduced to a terminating series [10]. We discuss the case $a > 0$ with $u' = E/RT'$. Equation (3) can be written as

$$J(u) = (E/R)^{a+1} \int_u^{\infty} u'^{-a-2} \exp(-u')\, \mathrm{d}u' \tag{4}$$

Making the substitution $u' = tu$, eqn. (4) can be recast into

$$J(u) = (E/Ru)^{a+1} \int_1^{\infty} \exp(-tu) t^{-a-2}\, \mathrm{d}t \tag{5}$$

Now using the relation

$$\int_1^{\infty} \exp(-tu) t^{-a-2}\, \mathrm{d}t = E_{a+2}(u) \tag{6}$$

where $E_m(u)$ is the exponential integral [12], eqn. (5) can be expressed as

$$J(u) = Ef(u)/R \tag{7}$$

0040-6031/91/$03.50

TABLE 1

Comparison of the values of exponential integrals

u	$(u+2)E_2(u)\exp(u)$		$(u+4)E_4(u)\exp(u)$	
	This work	Ref. 12	This work	Ref. 12
2	1.10937	1.10937	1.10937	1.10937
5	1.03522	1.03522	1.04584	1.04584
10	1.01240	1.01240	1.01889	1.01889
20	1.00384	1.00384	1.00654	1.00654
25	1.00258	1.00258	1.00451	1.00451
50	1.00071	1.00071	1.00133	1.00133
100	1.00019	1.00019	1.00036	1.00036

with

$$f(u) = \frac{E_{a+2}(u)}{u^{a+1}} \tag{8}$$

Let us first take up the most commonly occurring case where $a = 0$. From eqns. (7) and (8) we get for $a = 0$

$$J(u) = EE_2(u)/Ru \tag{9}$$

Following Gaustchi and Cahill [12], $E_2(u)$ can be approximated as follows. For $0 \leqslant u \leqslant 1$

$$E_2(u) = \exp(-u) - u\left(a_0 + a_1 u + a_2 u^2 + a_3 u^3 + a_4 u^4 + a_5 u^5\right) \tag{10}$$

where $a_0 = -0.577216$, $a_1 = 0.999992$, $a_2 = 0.249911$, $a_3 = 0.05520$, $a_4 = -0.009670$ and $a_5 = 0.001079$, whereas for $u > 1$, we have [12]

$$\exp(u)E_2(u) = \frac{0.999993u^3 + 7.5739u^2 + 12.464892u + 3.690723}{u^4 + 9.573322u^3 + 25.632956u^2 + 21.099653u + 3.958479} \tag{11}$$

In Table 1 we compare [6], the values of $(u+2)E_2(u)\exp(u)$ computed by employing the approximation to $E_2(u)$ used by us with the values tabulated in ref. 12. We find that the agreement is excellent. We now proceed with the evaluation of $I(T_1, T_2)$ for both small and large temperature intervals. We study the following two cases; (i) $T_1 = 500$ K, $T_2 = 516$ K and $E = 22$ kcal; and (ii) $T_1 = 500$ K, $T_2 = 600$ K and $E = 22$ kcal. From eqns. (2) and (8) we have

$$I(T_1, T_2) = T_2^{a+1}E_{a+2}(E/RT_2) - T_1^{a+1}E_{a+2}(E/RT_1) \tag{12}$$

For $a = 0$, eqn. (12) reduces to

$$I(T_1, T_2) = T_2E_2(E/RT_2) - T_1E_2(E/RT_1) \tag{13}$$

We have also evaluated $I(T_1, T_2)$ numerically using Simpson's 1/3 rule [13] for cases (i) and (ii). It is to be noted that case (i) has also been

TABLE 2
Comparison of the values of $I(T_1, T_2)$

a	$I(T_1, T_2)$ [a]			$I(T_1, T_2)$ [b]	
	This work	Ref. 14	Numerical result	This work	Numerical result
0	5.575(−9) [c]	5.576(−9)	5.575(−9)	2.802(−7)	2.802(−7)
2	1.444(−3)		1.444(−3)	9.265(−2)	9.265(−2)

[a] $T_1 = 500$ K, $T_2 = 516$ K, $E = 22$ kcal.
[b] $T_1 = 500$ K, $T_2 = 600$ K, $E = 22$ kcal.
[c] $a(-b)$ stands for $a \times 10^{-b}$.

considered by Urbanovici and Segal [14] and their numerical result is in very good agreement with ours. We see from Table 2 that in both the cases the values of the integrals computed by the present method are in close agreement with the numerical results.

Finally we observe that the present method can be readily extended to the case $a > 0$. For $m > 2$ the computation of $E_m(u)$ present some problems. For $0 \leqslant u \leqslant 10$ we have computed $E_m(u)$ $(m > 2)$ starting from eqns. (10) and (11) for $E_2(u)$ by using the forward recursion relation [12]:

$$E_m(u) = \frac{1}{(m-1)}\left[\exp(-u) - uE_{m-1}(u)\right] \tag{14}$$

For $u > 10$ the use of the forward recursion relation in the evaluation of $E_m(u)$ $(m > 2)$ leads to significant errors. We have adopted the following procedure for the evaluation of $E_m(u)$ $(m > 2)$ for $u > 10$. We started our evaluation using the relation [12]

$$E_m(u) = \frac{\exp(-u)}{(u+m)}\left[1 + \frac{m}{(u+m)^2} + \frac{m(m-2u)}{(u+m)^4} + \frac{m(6u^2 - 8mu + u^2)}{(u+m)}\right] \tag{15}$$

by putting $m = 10$ and computed $E_m(u)$ $(m > 2)$ by using the backward recursion relation

$$E_m(u) = \frac{1}{u} - \left[\exp(-u) - mE_{m+1}(u)\right] \tag{16}$$

As an example, let us consider the case $a = 2$ which may occur in some thermally stimulated processes [14]. For $a = 2$, eqn. (12) can be written as

$$I(T_1, T_2) = T_2^3 E_4(E/RT_2) - T_1^3 E_4(E/RT_1) \tag{17}$$

We find from Table 1 that the values of $(u+4)E_4(u)\exp(u)$ computed by the present method are in very good agreement with those tabulated in ref. 12.

Finally in this case also we consider the evaluation of $I(T_1, T_2)$ for both small and large temperature intervals as for $a = 0$. It is evident from Table 2 that for $a = 2$ the values of $I(T_1, T_2)$ computed by employing the present method agree very well with values obtained numerically.

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