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EVALUATION OF TEMPERATURE INTEGRAL FOR TEMPERATURE DEPENDENT FREQUENCY FACTORS

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Abstract

The general method of evaluating the temperature integral for temperature dependent frequency factors have been considered. The values of the temperature integral as evaluated by the present method are in excellent agreement with those obtained numerically.

Keywords: temperature integral

Introduction

The determination of kinetic data from DTA and TG curves requires an accurate evaluation of temperature integral namely

$$I_a(T) = \int_0^T T^a \exp(-E/RT)\mathrm{d}T \tag{1}$$

The evaluation of temperature integral for the case of temperature independent frequency factor has been studied extensively [1]. But the evaluation of temperature integral is also required for the case $a \neq 0$ [2], where a can be positive or negative integers and half-integers House [3, 4], House and Daniel House [5] discussed the numerical evaluation of the temperature integral for different values of a. In the present note we have proposed a general method for analytical evaluation of temperature integral both for the positive and negative integer and half-integer values of a.

Discussion

In order to determine activation energy (E) from DTA and TG curves one requires the evaluation of I_a (T) for different values of T [6]. If I_a is evaluated nu-

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merically then for an accurate determination of E the numerical evaluation is to be carried out by using small step size and by partitioning the interval (0, T) into a number of subranges thereby requiring a good amount of computer time. In order to avoid this difficulty derived analytical expressions for $I_a(T)$ have been used because these expressions require less computer time and give a reasonable accuracy [1]. Putting $u=E/RT$ the temperature integral (1) can be expressed as

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

Now by using the definition of the complementary incomplete Gamma function [7]

$$\Gamma(a,x) = \int_x^{\infty} \mathrm{e}^{-t}t^{a-1}\mathrm{d}t \tag{3}$$

I_a (u) can be written as

$$I_a(u) = (E/R)^{a+1}\Gamma(-a-1,\, u) \tag{4}$$

Now we consider the following cases.

Case I:

a is an integer greater than or equal to -1. For this case $I_a(u)$ can be expressed in terms of exponential integral [4] by virtue of the relation

$$E_n(u) = u^{n-1}\Gamma(1-n,\, u) \tag{5}$$

that is

$$I_a(u) = (E/Ru)^{a+1}E_{a+2}(u) \tag{6}$$

The evaluation of $E(u)$ $(a \geq 2)$ can be carried out by using the recursion relation [7]

$$E_{n+1}(x) = [\exp(-x) - xE_n(x)]/n \quad (n=1,\, 2,\, 3,\, \ldots.) \tag{7}$$

by starting with a rational approximation for $E_1(x)$ given by [7]

$$E_1(x) = [f(x)/x\, g(x)]\exp(-x) \quad (1 \le x \le \infty) \tag{8}$$

with

$$f(x) = x^4 + 8.573329x^3 + 18.059017x^2 + 8.634761x + 0.267774 \tag{9}$$

$$g(x) = x^4 + 9.573322x^3 + 25.632956x^2 + 21.099653x + 3.958497 \tag{10}$$

and

$$E(x) = -\ln(x) - 0.577216 + 0.999992x - 0.249911x^2 + 0.055200x^3 - 0.009760x^4 + 0.001079x^5 \quad (0 \le x \le 1) \tag{11}$$

Case II:

a is a positive or negative half integer $a=m+1/2$, where m is a positive or a negative integer including 0. Now Eq. (4) can be expressed as

$$I_{m+1/2}\,(u) = (E/R)^{m+3/2}\Gamma(-\,m - 3/2,\, u) \tag{12}$$

For $m=-2$

$$I_{-3/2}(u) = (E/R)^{-1/2}\Gamma\,(1/2,\, u) \tag{13}$$

It is well known that [7]

$$\Gamma\,(1/2,\kappa) = \sqrt{\pi}\,\mathrm{erfc}(\sqrt{\kappa}) \tag{14}$$

where erfc(x) is the complementary error function [7]. For other values of m, $I_{m+\frac{1}{2}}(u)$ can be evaluated by using backward recursion relation [7]

$$\Gamma(a,\kappa) = [\Gamma(a+1,\kappa) - \kappa^a e^{-\kappa}]/a \tag{15}$$

For example, after the evaluation of $I_{-3/2}(u)$ using $\Gamma(1/2,\, u)$ one can use the recursion relation (15) with $a=1/2$ to generate $\Gamma(-\,1/2,\, u)$ required for the evaluation of $I_{-1/2}(u)$ and so on.

For $x\le 5$, we use a rational approximation [7] to erfc(x) given by

$$\mathrm{erfc}(x) = 1 - \mathrm{erf}(x) = (a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5)e^{-x^2} \tag{16}$$

where erf(x) is the error function and $t=1/(1+px)$ with

$p = 0.3275911,\ a_1 = 0.254829592,\ a_2 = -0.284496736,\ a_3 = 1.421413741,$

$a_4 = -1.453152027,\ a_5 = 1.061405429$

For $x > 5$ we have used the expression [7]

$$\mathrm{erfc}(x) = \exp(-x^2)\left[1 + \sum_{m+1}^{\infty}(-1)^m \frac{1\cdot 3\cdot 5\cdots(2m-1)}{(2x\ su2)^m}\right] \tag{17}$$

Case III:

$a=-2$. In this case the temperature integral can be evaluated exactly as

$$I_{-2}(u) = (R/E)\exp(-u) \tag{18}$$

Table 1 Comparison of numerical values of lg I_a with those obtained by using the present method

T/K	a	$-\log I_a$			
		E=40 kcal·mol^{-1}		E=60 kcal·mol^{-1}	
		Present	Numerical	Present	Numerical
	–3/2	24.86160	24.86159	35.96360	35.96360
	–1	23.56474	23.56474	34.66538	34.66538
	–1/2	22.26784	22.26784	33.36715	33.36715
400	0	20.97091	20.97091	32.06890	32.06890
	1/2	19.67394	19.67394	30.77062	30.77063
	1	18.37694	18.37694	29.47234	29.47234
	3/2	17.07989	17.07990	28.17404	28.17404
	2	15.78282	15.78282	26.87572	26.87572
	–3/2	13.78781	13.78781	19.42488	19.42488
	–1	12.34436	12.34436	17.97885	17.97885
	–1/2	10.90077	10.90077	16.53274	16.53274
800	0	9.45705	9.45705	15.08657	15.08657
	1/2	8.01321	8.01319	13.64034	13.64034
	1	6.56922	6.56922	12.19405	12.19405
	3/2	5.12496	5.12511	10.74768	10.74770
	2	3.68090	3.68089	9.30129	9.30129

It is to be noted that we have to use a double precision arithmetic for the accurate evaluation of the error function. We have also evaluated temperature integral numerically using Simpson's 1/3 rule [8, 9]. In order to achieve higher accuracy the numerical evaluation of the temperature integral has been performed by splitting the range (0, T) into a number of subranges [10]. In the present case the number of subranges is equal to 4 for $T=100$ K and equal to 8 for $T=800$ K. There is a good agreement between the values of $-\log I_a$ computed numerically by us with those reported in the literature [3–5]. In Table 1 we have compared the values of $-\log I_a$ evaluated analytically and numerically for E values equal to 40 and 60 kcal/mol and temperatures (T) 400 and 800 K. It is observed that the values of $-\log I_a$ are in good agreement with the numerical results.

Conclusion

We conclude that the present method can be used for the accurate and rigorous evaluation of the temperature integral required in the determination of the kinetic data from DTA and TG curves.

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Zusammenfassung — Es wurde eine allgemeine Methode zur Auswertung des Temperaturintegrales für temperaturabhängige Frequenzfaktoren betrachtet. Die Werte für die Temperaturintegrale nach vorliegender Methode stehen in ausgezeichneter Übereinstimmung mit den numerisch erhaltenen Werten.