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EVALUATION OF THE TEMPERATURE INTEGRAL BY PROGRAMMABLE CALCULATOR

J.E. HOUSE, JR.

Department of Chemistry, Illinois State University, Normal, IL 61761 (U.S.A.)

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ABSTRACT

In the analysis of TG curves to extract kinetic data approximation of the temperature integral must be made. Currently available programmable calculators and small computers make it possible to do numerical integration quickly and accurately as part of the kinetic treatment. It is necessary, however, to understand the limits of accuracy of the results and the factors affecting the computations. The results of several of these factors have been evaluated. The data presented provide a basis for evaluating and comparing such numerical methods.

INTRODUCTION

For a nonisothermal process, the rate law is frequently written as

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

where α is the fraction reacted, T is the temperature (K), R is the molar gas constant, E is the activation energy, β is the heating rate, and A is the pre-exponential factor. Typically, $f(\alpha)$ is taken as $(1-\alpha)^n$, where n is the reaction order so that

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} (1-\alpha)^n \tag{2}$$

or

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \tag{3}$$

Complete analysis of the TG curves is made difficult by the fact that the temperature integral, $\int_0^T e^{-E/RT} dT$ has no closed form equivalent. In order to deal with a number of important problems in nonisothermal kinetics it is essential that the temperature integral be evaluated accurately. Approximations of this integral by truncated series or other methods have resulted in the development of a number of computational and curve fitting approaches [1—19]. Tables of values for the integral are available for specified temperatures and activation energies [17] and approximation formulas have been derived [18].

The programmable calculator has found wide applicability in a variety of complex data analysis and computational procedures [20—24] and the computing power of the current generation of programmable calculators approaches that of the small computer. Evaluation of the temperature integral is easily carried out using any of the more sophisticated machines. The interactive capability of the machine is important as well. In developing an analysis procedure for TG curves for kinetic data, it was necessary to perform rapid evaluations of the temperature integral at any value of E and T. The purpose of this paper is to describe the evaluation of the temperature integral using a programmable calculator and to present some observations on the nature of the results which must be considered in using them in programs to evaluate kinetic data.

METHOD

The evaluation of the temperature integral was carried out using a Texas Instruments programmable TI-59 calculator with the PC-100C printer. In order to generate a table of values at regular values of T and E, a program was written to begin with a starting value of E, $T_0 = 0$, and a specified upper temperature limit. The program then increments the upper temperature limit to a higher value and then proceeds to evaluate the temperature integrals until all the desired values of T are used. Next the activation energy is incremented and the whole series of upper temperature limits used again. The program calls as a subroutine the Simpson's rule routine in the program read only memory (PROM). Any starting values for the upper limit of temperature and activation energy can be specified and any size increments in each can be chosen. The program computes the negative logarithm of the integral as the final output. A copy of the program with documentation is available from the author.

For single evaluations of the temperature integral the same approach was used with the library program for Simpson's rule integration. In both cases, the interval width (actually the number of subintervals) must be specified.

RESULTS AND DISCUSSION

Effect of the number of subintervals

In order to evaluate the requirements of the computations to give a desired accuracy in the $-\log I$ value it was necessary to determine the effect of varying the number of subintervals used in the integration. To do this, it was chosen to evaluate the integrals from 0 to 400 K for E = 30 kcal mole^{-1} and in the interval 0—800 K for $E = 80$ kcal mole^{-1} using $R = 1.9872$ cal mole^{-1} deg^{-1}. Although the specified data were assumed to be exact, when using this value of R the resulting integration cannot be accurate to all the

TABLE 1

Effect of the number of subintervals on computing time and accuracy of numerical integration of the temperature integral

No. of subintervals	Computing time (min)	$-\log I$	
		$E = 30$ kcal mole^{-1} ($T = 400$ K)	$E = 80$ kcal mole^{-1} ($T = 800$ K)
10	0.30	15.24048210	20.42439332
20	0.60	15.36721578	20.62094035
30	0.88	15.38286736	20.65845491
40	1.18	15.38601943	20.66729999
50	1.45	15.38693834	20.66780446
60	1.77	15.38727866	20.66885229
100	2.85	15.38756119	20.66974319
200	5.72	15.38760152	20.66987322
400	11.38	15.38760406	20.66988149
1000	28.53	15.38760422	20.66988203
1600	45.00	15.38760423	20.66988204
Lit. [a]		15.387604	20.669882

[a] From ref. 17.

digits displayed even though they are kept here to show the complete output and convergence. The most accurate published values for $-\log I$ under these two sets of conditions are 15.387604 and 20.669882, respectively [17].

Of course, as the number of subintervals used in the integration increases, so does the computing time. Table 1 shows the results of varying the number of subintervals on the accuracy of $-\log I$ and computing time. As the integration is carried out over a longer range of temperature, an increasing number of subintervals must be used to provide the same accuracy. For example, for $T_0 = 0$ and $T = 400$ K with $E = 30$ kcal mole^{-1}, the published value of $-\log I$ is obtained by a 100 subinterval integration. For the $T_0 = 0$ and $T = 800$ K with $E = 80$ kcal mole^{-1} case, the 100 subinterval integration gives an error of only -0.0002, and the 200 subinterval integration gives four decimal place agreement with the published value. The values shown in Table 1 show that a 400 subinterval integration reproduces the six decimal value in the shorter temperature interval, but a 1000 subinterval one is required to reproduce all six decimal places in the longer temperature integration. It is readily apparent that the approach used can reproduce the results obtained using a computer at the sacrifice of speed. However, the interactive nature of the programmable calculator permitting instant selection of parameters, its availability, and its portability make it a viable alternative for these calculations.

Probably the best compromise of accuracy and computing time is afforded by the 60 or 100 subinterval computations. The values of $-\log I$ are accurate enough for most purposes and the computing time is reasonably short. This is especially true since iterative processes to evaluate n and E are carried out using differences between the values of the integrals at several upper temperature limits close together. Therefore, the integrations must be reasonably accurate but rapidly carried out. In the interest of accuracy, all subsequent integrations in this work were carried out using the 200 subinterval integrations. The values obtained when a 1000 or 1600 subinterval integration is used provide more accurate values of $-\log I$ than those previously published.

Acceleration of convergence

In view of the length of time necessary to compute the value of the integrals when a large number of subintervals are used, it became apparent that a more rapid method of convergence was desirable. Utilizing this approach, several less accurate values could be obtained from integrations with a smaller number of intervals and these in turn could be subjected to a numerical convergence procedure. One such procedure is the Romberg Algorithm [25], and a program for carrying it out on a programmable calculator has been published [20]. This technique produces rapid convergence of a series of values obtained when different numbers of integration steps are used, thus avoiding lengthy integrations.

A series of values for $-\log I$ when $E = 30$ kcal mole^{-1} and $T = 400$ K is given in Table 1. To test the applicability of the Romberg Algorithm the values obtained using 10, 20, 30, 40, and 50 subintervals were subjected to the Romberg calculation. The result was a value $-\log I = 15.38726128$, which is only slightly more accurate than the value obtained using the 50 subinterval integration alone. When the $-\log I$ values obtained using 30, 40, 50, 60, and 100 subinterval integrations were used in the Romberg acceleration method, $-\log I = 15.38767829$ resulted. The value for 100 subintervals is 15.38756119 so there is almost no improvement obtained by using values with fewer subintervals and then converging them by the Romberg technique. Similar results were obtained using the data when $E = 80$ kcal mole^{-1} and $T = 800$ K data in Table 1. It appears that in the case of the temperature integral there is not enough improvement to warrant the additional computation. A better result is obtained by simply increasing the number of integration subintervals.

Accuracy variation with E *and* T

Since using a definite number of integration steps produces a somewhat different effect on $-\log I$ depending on the values of E and T, it was necessary to study a broad range of values for these parameters. The range selected was chosen to include the most practical values of E (30—100 kcal mole^{-1}) and upper temperature limit (300—1000 K) normally encountered in TG work. Table 2 shows the results produced using a 200 subinterval integration. Each integral required about 6 min to evaluate so that Table 2 represents about 6 h of unattended computation. The values of $-\log I$ are rounded to six decimal places so that they can be compared directly with the standard reference compilation [17]. A comparison shows that the data in

TABLE 2

Values of $-\log \int_0^T e^{-E/RT}\, dT$ for various values of T and E [a] using 200 subintervals

T (K)	$-\log I$							
	$E = 30$	$E = 40$	$E = 50$	$E = 60$	$E = 70$	$E = 80$	$E = 90$	$E = 100$
300	21.095842	28.501585	35.880858	43.243174	50.593674	57.935449	65.270501	72.600199
400	15.387602	20.970903	26.528222	32.068850	37.597838	43.118236	48.632025	54.140569
500	11.920756	16.410141	20.873993	25.321398	29.757309	34.184730	38.605620	43.021326
600	9.581986	13.341738	17.076385	20.794812	24.501883	28.200555	31.892759	35.579828
700	7.891996	11.130295	14.343895	17.541492	20.727865	23.905924	27.077575	30.244135
800	6.610078	9.457047	12.279706	15.086572	17.882338	20.669873	23.451057	26.227192
900	5.601917	8.144317	10.662778	13.165647	15.657538	18.141277	20.618721	23.091154
1000	4.786578	7.085150	9.360137	11.619726	13.868456	16.109111	18.343523	20.572963

[a] kcal mole^{-1}.

TABLE 3

Effect of changing the lower limit with a 200 step integration (E = 30 kcal mole^{-1}; T(upper) = 400 K)

Lower limit (K)	—log I
0	15.38760152
10	15.38760178
25	15.38760213
50	15.38760264
100	15.38760337
200	15.38760406
300	15.38760507
350	15.38913047

Table 2 are accurate to all six decimal places at the lower values of E and higher upper temperature limits, and agreement is to at least three decimals except for $E = 90$ or 100 kcal mole^{-1} and $T = 300$ K. The largest error in —log I, about 0.001, occurs with the highest E values and at the lowest values of T. Other than those few combinations, agreement is, for the most part, to at least four decimal places. More accurate values could have been obtained using a larger number of subintervals. For example, the published value for —log I when $E = 100$ kcal mole^{-1} and $T = 400$ K is reproduced exactly with a 1000 subinterval integration. Since the purpose of these calculations was to show that suitable accurate values of the temperature integral could be obtained in a reasonable time, this approach was not used.

Effect of change in lower limit

In certain computations, it is necessary to know the difference between $\int_0^T e^{-E/RT}\,dT$ and $\int_{T_0}^T e^{-E/RT}\,dT$, where T_0 is some lower limit other than 0 K. Accordingly, a program was written to systematically vary the lower limit, T_0, while keeping the upper limit at 400 K and the integration subintervals at 200. The results of evaluating this series of integrals is shown in Table 3. From the results, it is readily apparent that even when the lower limit is 300 K no serious error is introduced. In fact, the integral evaluates to 15.3876 for any lower limit in the range 0—300 K. Clearly, if there is some reason to evaluate the integral with some lower limit than 0 K no significant error is introduced if the number of integration subintervals is large. This can be of importance with some programmable calculators since underflow can occur with the large negative value of the exponent when T is small halting computation. Changing the lower limit can prevent this and as can be seen from Table 3, no substantial error is introduced.

Linear relationships

It has been observed that the relationships

$$-\log I = ME + B \qquad \text{(at constant } T\text{)} \tag{4}$$

TABLE 4

Linear regression parameters for $-\log I = ME + B$ at constant temperature

Temp. (K)	Slope(M)	—Intercept(B)	Corr. coeff.
300	0.7355826	0.9227061	0.999999
400	0.5534231	1.1669716	0.999998
500	0.4441065	1.3550171	0.999997
600	0.3712138	1.5076531	0.999995
700	0.3191355	1.6359112	0.999994
800	0.2800668	1.7463596	0.999992
900	0.2496715	1.8432292	0.999990
1000	0.2253479	1.9294061	0.999988

TABLE 5

Linear regression parameters for $-\log I = N(1/T) + D$ at constant E

E (kcal mole^{-1})	Slope(N)	—Intercept(D)	Corr. coeff.
30	6987.804	2.122092	0.999945
40	9176.508	2.011027	0.999967
50	11364.005	1.922756	0.999978
60	13550.849	1.849458	0.999985
70	15737.295	1.786755	0.999988
80	17923.470	1.731943	0.999991
90	20109.447	1.683230	0.999993
100	22295.266	1.639364	0.999994

and

$$-\log I = N(1/T) + D \qquad \text{(at constant } E\text{)} \tag{5}$$

where M, N, B, and D are constants, provide accurate approximations of $-\log I$ in terms of E and T, respectively [18]. Also, it was reported that the slopes and intercepts could themselves be obtained as functions of E and T [18]. These linear relationships have been investigated, and Tables 4 and 5 show the regression parameters for fitting the data obtained in this work to eqns. (4) and (5). It is readily apparent that by using these parameters it is a simple matter to quickly use a programmable calculator to produce values for the temperature integral at any values of T and E that are sufficiently accurate for all practical purposes.

SUMMARY

This work has shown that it is feasible to perform numerical integration of the temperature integral with a pocket programmable calculator to provide accurate values that can be used in a data analysis method that does not approximate the integral by a truncated series. The fact that the computing

machinery is completely interactive and portable frees one from the "fixed" values of the data presented in published tables. Acceleration of the integral convergence using the Romberg Algorithm does not improve the integration materially. Regression parameters have been determined for the —log I relationships with E and $1/T$.

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