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NUMERICAL RELATIONSHIPS FOR TEMPERATURE INTEGRALS WITH TEMPERATURE DEPENDENT FREQUENCY FACTORS

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ABSTRACT

Temperature integrals having a negative exponent (m) on temperature have been evaluated for $m = -1/2$, -1, $-3/2$, and -2 with $E = 30$–100 kcal mole^{-1} and $T = 300$–1000 K. For a given value of m, $-\log I$ is linearly related to E and $1/T$. The slopes and intercepts of these linear equations have been found to be functions of E and T. Also, a linear relationship exists between $-\log I$ and m for given values of E and T. By combining these results with those previously published for temperature integrals having positive values of m, equations have been obtained that permit accurate evaluation of temperature integrals for any combination of m, E, and T values.

INTRODUCTION

Integrals of the form

$$I = \int_0^T T^m \, e^{-E/RT} \, dT \qquad (1)$$

where T is the temperature (K), E is the activation energy, R is the molar gas constant, and m is a constant, 0, $\pm 1/2$, ± 1, $\pm 3/2$, ± 2, etc., arise in the treatment of kinetic data from non-isothermal studies [1]. There has been a great deal of interest in evaluating these integrals for many years. Approaches include numerical integration [2,3], approximation by series [4–8], evaluation by small computer [9] or a programmable calculator [10,11], and graphical methods [12]. Each of these methods possesses some advantages for certain applications. In our recent studies, evaluation of the case with temperature independent frequency factor ($m = 0$) [10] and temperature dependent frequency factor cases ($m = 1/2$, 1, 3/2, and 2) [11] were evaluated. It was also shown that by choosing specific values for E and T, the resulting $-\log I$ values gave linear relationships with m. In the present work, we have evaluated the integrals where m has negative values ($m = -1/2$, -1, $-3/2$, and -2). Using these results and those from the previous studies, we now have values for $-\log I$ using nine values of m from -2 to $+2$. Therefore, it has been possible to determine quite accurately the dependence of $-\log I$ on a range of m values and this report presents the results of that work. We have, therefore, now completed a comprehensive set of tables of integrals and numerical relationships.

METHODS

Evaluations of temperature integrals for $m = 0$, 1/2, 1, 3/2, and 2 were previously carried out using a Texas Instruments TI-59 Programmable calculator [10,11]. In this work, the integrals for $m = -1/2$, -1, $-3/2$, and -2 were evaluated using a Hewlett-Packard HP-34C calculator employing the three-digit scientific notation accuracy (f SCI 3) [13]. This instrument has a built-in numerical integration algorithm that calls as a subroutine the previously entered sequence to evaluate the function being integrated. The HP-34C was used because the algorithm that it uses provides greater accuracy in a shorter time than does the Master Library Simpson's rule program of the TI-59. For example, the three-digit scientific notation format with the HP-34C gives a result of $-\log I = 15.38760326$ in about 2.6 min for the case with $m = 0$, $E = 30$ kcal mole^{-1}, and $T = 400$ K. The TI-59 requires a 300 subinterval Simpson's rule computation and requires about 8.4 min to provide a result this close to the actual value of 15.38760423. Consequently, the HP-34C enables a greater accuracy to be obtained in a shorter computing time and it was used for all the numerical integrations in this work. As is true with the TI-59, a greater accuracy can be obtained, but at the sacrifice of computing speed. Linear regression was carried out as previously described [11].

RESULTS AND DISCUSSION

Numerical integration

In the analysis of non-isothermal kinetic data, the values of the temperature integral are needed [1–3]. These can be expressed either in the form

$$I = \int_0^T T^m \, e^{-E/RT} \, dT \tag{1}$$

or the expressions involving Euler's integral [14–16]. In our previous work, temperature integrals were evaluated for $m = 0$ and for positive values of m. In order to complete the set of numerical tables to include negative m values [17,18], we have performed numerical integration of cases where $m = -1/2$, -1, $-3/2$, and -2. The results of these evaluations are shown in Tables 1–4. Because of the integration procedure used, most of these values of $-\log I$ are accurate to the full number of decimal places shown. Previously, it was found that for $E = 100$ kcal mole^{-1} and

TABLE I

Values of $-\log \int_0^T T^m \mathrm{e}^{-E/RT} \mathrm{d}T$ for $m=-1/2$

T (K)	$-\log I$ $E=30$ kcal mole^{-1}	$E=40$ kcal mole^{-1}	$E=50$ kcal mole^{-1}	$E=60$ kcal mole^{-1}	$E=70$ kcal mole^{-1}	$E=80$ kcal mole^{-1}	$E=90$ kcal mole^{-1}	$E=100$ kcal mole^{-1}
300	22.33031	29.73706	37.11698	44.47978	51.83069	59.17287	66.50836	73.83857
400	16.68326	22.26784	27.82598	33.36715	38.89656	44.41731	49.93141	55.44026
500	13.26362	17.75457	22.21939	26.66747	31.10389	35.53167	39.95287	44.36885
600	10.96324	14.72481	18.46059	22.17980	25.88745	29.58655	33.27910	36.96647
700	9.30555	12.54592	15.76082	18.95930	22.14633	25.32489	28.49695	31.66385
800	8.05153	10.90077	13.72488	16.53274	19.32924	22.11733	24.89896	27.67546
900	7.06781	9.61274	12.13280	14.63677	17.12946	19.61382	22.09175	24.56459
1000	6.27426	8.57558	10.85232	13.11311	15.36272	17.60405	19.83900	22.06887

TABLE 2

Values of $-\log \int_0^T T^m \mathrm{e}^{-E/RT}\,\mathrm{d}T$ for $m=-1$

T (K)	$-\log I$ $E=30$ kcal mole^{-1}	$E=40$ kcal mole^{-1}	$E=50$ kcal mole^{-1}	$E=60$ kcal mole^{-1}	$E=70$ kcal mole^{-1}	$E=80$ kcal mole^{-1}	$E=90$ kcal mole^{-1}	$E=100$ kcal mole^{-1}
300	23.56474	30.97251	38.35302	45.71623	53.05943	60.40984	67.74551	75.07585
400	17.97885	23.56474	29.12367	34.66543	40.19519	45.71623	51.23056	56.73959
500	14.60640	19.09894	23.56474	28.01349	32.45039	36.87853	41.30002	45.71623
600	12.34436	16.10781	19.84475	23.56474	27.27296	30.97249	34.66543	38.35302
700	10.71893	13.96144	17.17767	20.37706	23.56474	26.74380	29.91625	33.08346
800	9.49271	12.34436	15.16996	17.97885	20.77608	23.56474	26.34681	29.12367
900	8.53342	11.08099	13.60270	16.10781	18.60133	21.08631	23.56474	26.03797
1000	7.76161	10.06582	12.34436	14.60639	16.85691	19.09893	21.33443	23.56474

TABLE 3

Values of $-\log \int_0^T T^m \mathrm{e}^{-E/RT}\,\mathrm{d}T$ for $m=-3/2$

T (K)	$-\log I$ $E=30$ kcal mole^{-1}	$E=40$ kcal mole^{-1}	$E=50$ kcal mole^{-1}	$E=60$ kcal mole^{-1}	$E=70$ kcal mole^{-1}	$E=80$ kcal mole^{-1}	$E=90$ kcal mole^{-1}	$E=100$ kcal mole^{-1}
300	24.79913	32.20789	39.58904	46.95267	54.30418	61.64681	68.98265	76.31313
400	19.27437	24.86160	30.42134	35.96364	41.49380	47.01514	52.52970	58.03892
500	15.94907	20.44324	24.91005	29.35947	33.79686	38.22537	42.64715	47.06359
600	13.72534	17.49072	21.22885	24.94964	28.65844	32.35841	36.05169	39.73956
700	12.13213	15.37686	18.59445	21.79477	24.98311	28.16268	31.33553	34.50306
800	10.93366	13.78781	16.61495	19.42488	22.22288	25.01211	27.79463	30.57186
900	9.99873	12.54907	15.07250	17.57876	20.07313	22.55876	25.03769	27.51133
1000	9.24861	11.55584	13.83626	16.09958	18.35103	20.59376	22.82980	25.06056

TABLE 4

Values of $-\log \int_0^T T^m \mathrm{e}^{-E/RT}\,\mathrm{d}T$ for $m = -2$

T	$-\log I$							
(K)	$E=30$ kcal mole^{-1}	$E=40$ kcal mole^{-1}	$E=50$ kcal mole^{-1}	$E=60$ kcal mole^{-1}	$E=70$ kcal mole^{-1}	$E=80$ kcal mole^{-1}	$E=90$ kcal mole^{-1}	$E=100$ kcal mole^{-1}
300	26.03347	33.44328	40.82505	48.18910	55.54091	62.88376	70.21978	77.55040
400	20.56982	26.15841	31.71898	37.26184	42.79240	48.31404	53.82884	59.33824
500	17.29164	21.78749	26.25532	30.70543	35.14329	39.57220	43.99427	48.41095
600	15.10618	18.87355	22.61289	26.33450	30.04389	33.74433	37.43793	41.12608
700	13.54513	16.79216	20.01115	23.21242	26.40145	29.58153	32.75478	35.92264
800	12.37435	15.23112	18.05985	20.87085	23.66963	26.45944	29.24243	32.02001
900	11.46375	14.01697	16.54217	19.04964	21.54487	24.03115	26.51059	28.98465
1000	10.73526	13.04569	15.32803	17.59267	19.84507	22.08852	24.32514	26.55635

$T=300$ K, the integration with $m=0$ using the TI-59 with a 200 subinterval integration gave $-\log I=72.60020$ compared with a previously reported value of 72.60144 [2]. This combination of E and T resulted in the least accurate $-\log I$ values [10]. Using the HP-34C with the accuracy level specified earlier, the value obtained is $-\log I=72.60128$. Consequently, the largest error in Tables 1–4 (which occurs with $E=100$ kcal mole^{-1} and $T=300$ K) is about 0.00016 and the error decreases rapidly for other combinations representing lower E and/or higher T values.

Dependence of $-\log I$ on E and $1/T$

It was previously shown that values of $-\log I$ obey the relationships

$$-\log I=ME+B \tag{2}$$

and

$$-\log I=N(1/T)+D \tag{3}$$

where, M, B, N and D are constants [3,11]. Thus, these constants have been determined for cases where $m=0$ [3,10] and $m=1/2$, 1, 3/2, and 2 [11]. In this work, we have established eqns. (2) and (3) for negative values of m by relating $-\log I$ to E and $1/T$ by linear regression. Tables 5 and 6 present the regression parameters for these equations. From the data presented and those previously published [11], it is readily apparent that there is no significant difference in the behaviour of $-\log I$ values obtained where m has negative values.

Equations relating slopes and intercepts

Gyulai and Greenhow [3] reported that the slopes and intercepts in eqns. (2) and (3) varied in such a way that they could be related to E and $1/T$. Thus, for eqn. (2)

$$M=K(1/T)^L \tag{4}$$

and

$$B=P\log(1/T)+Q \tag{5}$$

where K, L, P, and Q are constants. This approach was subsequently used for the $-\log I$ values where m has positive values [11]. The slopes and intercepts obtained with the negative m values used in this work were also studied in this way so that the equation

$$-\log I=K(1/T)^L E+\log(1/T)^P+Q \tag{6}$$

can be used for negative m values as well. Table 7 shows the values of K, L, P, and Q obtained by means of linear regression for each of the m values.

The slope and intercept in eqn. (3) were found to vary as

$$N=YE^X \tag{7}$$

and

$$D=W\log E+U \tag{8}$$

TABLE 5

Linear regression parameters for $-\log \int_0^T T^m \mathrm{e}^{-E/RT}\,\mathrm{d}T = ME + B$

T (K)	$m=-1/2$			$m=-1$		
	Slope (M)	Intercept (B)	Corr. Coeff.	Slope (M)	Intercept (B)	Corr. Coeff.
300	0.735634	0.310591	0.999999	0.735662	1.544084	0.999999
400	0.553476	0.127750	0.999998	0.553526	1.422602	0.999998
500	0.444168	−0.013148	0.999996	0.444229	1.328698	0.999996
600	0.371285	−0.127538	0.999995	0.371357	1.252468	0.999995
700	0.319217	−0.223670	0.999993	0.319300	1.188432	0.999993
800	0.280158	−0.306375	0.999992	0.280251	1.133356	0.999991
900	0.249772	−0.378945	0.999990	0.249875	1.085038	0.999989
1000	0.225457	−0.443489	0.999987	0.225570	1.042069	0.999987

where Y, X, W, and U are constants [3,11]. Thus, the equation

$$-\log I = YE^{X}(1/T) + \log E^{W} + U \tag{9}$$

expresses the complete dependence of $-\log I$ on E and $1/T$. The constants Y and X of eqn. (7) as well as W and U of eqn. (8) were obtained by linear regression establishing eqn. (9) for negative m values. Values of these constants for each value of m are shown in Table 7. The data shown in Table 7 permit eqns. (6) and (9) to be used to calculate values of $-\log I$ at any desired value of E and T at $m=-1/2$, -1, $-3/2$, and -2. These results combined with those previously published enable calculations of $-\log I$ to be made at any fixed integer or half-integer value of m from -2 to $+2$.

TABLE 6

Linear regression parameters for $-\log \int_0^T T^m \mathrm{e}^{-E/RT}\,\mathrm{d}T = N(1/T) + D$

E (kcal mole^{-1})	$m=-1/2$			$m=-1$		
	Slope (N)	Intercept (D)	Corr. Coeff.	Slope (N)	Intercept (D)	Corr. Coeff.
30	6879.76	−0.546253	0.999968	6771.84	1.029191	0.999985
40	9067.74	−0.431978	0.999981	8959.04	1.146850	0.999991
50	11254.78	−0.341678	0.999988	11145.57	1.239278	0.999994
60	13441,32	−0.267005	0.999991	13331.77	1.315406	0.999996
70	15627.56	−0.203325	0.999993	15514.97	1.384121	0.999997
80	17813.62	−0.147816	0.999995	17703.62	1.436470	0.999998
90	19999.55	−0.098606	0.999996	19889.39	1.486326	0.999998
100	22185.39	−0.054415	0.999997	22075.11	1.531025	0.999999

$m=-3/2$			$m=-2$		
Slope (M)	Intercept (B)	Corr. Coeff.	Slope (M)	Intercept (B)	Corr. Coeff.
0.735710	2.778270	0.999999	0.735749	4.012050	0.999999
0.553576	2.717368	0.999998	0.553627	4.012055	0.999997
0.444291	2.670427	0.999996	0.444354	4.012048	0.999996
0.371431	2.632329	0.999995	0.371506	4.012039	0.999994
0.319384	2.600338	0.999993	0.319471	4.012027	0.999992
0.280346	2.572831	0.999991	0.280445	4.012041	0.999990
0.249981	2.548700	0.999988	0.250091	4.012049	0.999988
0.225687	2.527250	0.999986	0.225808	4.012069	0.999985

Relationship between −log I and m

It was previously shown that for a given combination of E and T there is a linear relationship between $-\log I$ and m, viz.

$$-\log I = Am + C \tag{10}$$

where A and C are constants [11]. Having previously shown that such relationships exist, a major objective of this work was to use the extended series of m values to fully establish these relationships. By combining the previous results with those obtained in this work, a total of nine values of m (0, $\pm 1/2$, ± 1, $\pm 3/2$, and ± 2) can now be related to $-\log I$ through linear regression for constant values of E and T. For the first time, it is possible to use this large number of data points to establish

$m=-3/2$			$m=-2$		
Slope (N)	Intercept (D)	Corr. Coeff.	Slope (N)	Intercept (D)	Corr. Coeff.
6664.05	2.604239	0.999996	6556.38	4.178884	1.000000
8850.40	2.725461	0.999998	8741.83	4.303834	1.000000
11036.41	2.820085	0.999999	10927.30	4.400729	1.000000
13222.25	2.897709	0.999999	13112.76	4.479903	1.000000
15407.97	2.963545	0.999999	15289.22	4.546855	1.000000
17593.64	3.020693	0.999999	17483.67	4.604851	1.000000
19779.26	3.071195	1.000000	19669.13	4.656016	1.000000
21964.84	3.116423	1.000000	21854.59	4.701776	1.000000

TABLE 7

The constants of eqns. (6) and (9) obtained by linear regression

m	Equation (6)				Equation (9)			
	K	*L*	*P*	*Q*	*X*	*Y*	*W*	*U*
−1/2	199.150	0.98228	1.44208	3.88052	0.97309	250.578	0.40903	−1.94006
−1	198.663	0.98186	0.96027	3.92140	0.98187	239.611	0.41766	−0.39298
−3/2	198.243	0.98149	0.48007	3.96665	0.99086	228.919	0.42560	1.15576
−2	197.796	0.98110	0.00000	4.01204	0.99993	218.593	0.43430	2.70174

TABLE 8

Slopes (A) and intercepts (C) for fitting $-\log \int_0^T T^m \mathrm{e}^{-E/RT}\, \mathrm{d}T = Am + C$

T (K)		$E=30$ kcal mole^{-1}	$E=40$ kcal mole^{-1}	$E=50$ kcal mole^{-1}	$E=60$ kcal mole^{-1}	$E=70$ kcal mole^{-1}	$E=80$ kcal mole^{-1}	$E=90$ kcal mole^{-1}	$E=100$ kcal mole^{-1}
300	$-A$	2.46896	2.47093	2.47214	2.47298	2.47307	2.47411	2.47455	2.47495
	C	21.09572	28.50153	35.88084	43.24320	50.59287	57.93562	65.27079	72.60066
400	$-A$	2.59137	2.59390	2.59547	2.59655	2.59732	2.59792	2.59840	2.59881
	C	15.38739	20.97078	26.52816	32.06883	37.59783	43.11826	48.63210	54.14070
500	$-A$	2.68582	2.68890	2.69081	2.69212	2.69307	2.69379	2.69436	2.69483
	C	11.92044	16.40996	20.87387	25.32132	29.75727	34.18471	38.60562	43.02135
600	$-A$	2.76262	2.76622	2.76846	2.76999	2.77111	2.77196	2.77264	2.77317
	C	9.58155	13.34148	17.07621	20.79469	24.50180	28.20050	31.89273	35.57981
700	$-A$	2.82726	2.83135	2.83391	2.83566	2.83694	2.83792	2.83869	2.83932
	C	7.89143	11.12995	14.34367	17.54133	20.72775	23.90584	27.07752	30.24410
800	$-A$	2.88301	2.88756	2.89043	2.89240	2.89383	2.89493	2.89580	2.89650
	C	6.60937	9.45661	12.27941	15.08636	17.88218	20.64544	23.45097	26.22712
900	$-A$	2.93198	2.93698	2.94013	2.94231	2.94390	2.94512	2.94608	2.94687
	C	5.60105	8.14379	10.66242	13.16539	15.65734	18.14113	20.61860	23.09106
1000	$-A$	2.97561	2.98104	2.98447	2.98685	2.98860	2.98993	2.99087	2.99184
	C	4.78554	7.08078	9.35970	11.61941	13.86822	16.10893	18.34348	20.57284

the linear dependence of $-\log I$ on m. Table 8 shows the results of linear regression analysis to determine the constants A and C in eqn. (10). In each case, the correlation coefficient was exactly 1.00....

The results presented here and those presented in previous studies [11] permit any type of numerical analysis of temperature integrals to be made. Equations (6) and (9) and the constants given in Tables 5–7 permit computations of $-\log I$ at any values of E and T, not just those tabulated. Further, eqn. (10) and the computed constants for it shown in Table 8 permit evaluation of $-\log I$ for any value of m. Therefore, the means are now available to obtain a value for a temperature integral at any set of conditions that analysis of non-isothermal kinetics requires.

SUMMARY

The results of numerical integration are presented for temperature integrals having negative temperature exponents, m. For each value of m used ($-1/2$, -1, $-3/2$, and -2), $-\log I$ is linearly related to E and T. Linear regression was used to calculate the slopes and intercepts. These regression parameters were themselves analyzed as functions of E and T. By considering results presented here and in previous studies, equations are presented to relate $-\log I$ accurately to the value of m. Thus, $-\log I$ can now be computed for any value of E, T, and m.

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