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EVALUATION OF TEMPERATURE INTEGRALS FOR TEMPERATURE-DEPENDENT FREQUENCY FACTORS

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ABSTRACT

The temperature integrals of the form

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

where $m = 1/2$, 1, 3/2, and 2 have been evaluated for $T = 300$—800 K and $E = 30$—100 kcal mole^{-1}. The $-\log I$ values have been fitted to linear equations in E and $1/T$. Numerical equations have been obtained by treating the slopes and intercepts as functions of E and T. These equations permit evaluation of the integrals at any values of E and T. The functional dependence of $-\log I$ on the m value has also been investigated and linear relationships exist for given values of E and T.

INTRODUCTION

The approximation of the temperature integral

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

has received much attention in both theoretical [1—6] and practical [7—12] approaches. Tables of values [4] and approximate empirical equations [3] are available. However, it is of fundamental importance to realize that this integral is a result of assuming that Arrhenius behavior of the rate constant

$$k = A \, e^{-E/RT} \tag{2}$$

is observed. When A is not independent of temperature, it is possible, for many cases, to write

$$A = A_m T^m \tag{3}$$

so that the rate constant must be written as

$$k = A_m T^m \, e^{-E/RT} \tag{4}$$

where m is either an integer or half integer [13,14]. Recently, Segal [15] provided approximate analytical functions for these cases in which

$$I = \int_0^T T^m \, e^{-E/RT} \, dT \qquad (5)$$

where m is an integer or half integer. However, suitable tables of values for these integrals are either not extant or are of a fragmentary nature. It is the purpose of this paper to present the values for the integrals [eqn. (5)] for $m = 1/2$, 1, 3/2, and 2 and to determine empirical relationships for obtaining appropriate values of the integrals for any values of T and E as well as m.

METHOD

The numerical integrations of the integrals having the form of eqn. (5) were carried out as previously described to determine $-\log I$ [16]. For each value of m used, a series of computations were carried out for $T = 300$ K and $E = 30$ kcal mole^{-1} using 10, 20, 30, 40, 50, 100, 200, 400, and 1000 subintervals. The values obtained using 1000 subintervals appear to be correct to at least six decimal places [16]. At $E = 30$ kcal mole^{-1} and $T = 300$ K, the 200 subinterval integration gave values of $-\log I$ that agree with those of the 1000 subinterval integration to five decimal places. However, as was previously observed, the accuracy decreases at higher values of E. Therefore, it is likely that the values of $-\log I$ for the higher E values are accurate to four decimal places in some cases since a 200 subinterval integration was used in all cases.

Acceleration of convergence was determined by means of the Romberg algorithm [16,17]. This was carried out using the values of $-\log I$ obtained from 10, 20, 30, 40, and 50 subintervals.

Curve fitting to provide the empirical relationships between $-\log I$ and E and between $-\log I$ and $1/T$ was carried out using a program for a Texas Instruments TI-59 programmable calculator. Linear regression is carried out as a subroutine of that program. This approach was also used to obtain the equations in which the slopes and intercepts were treated as variables in T and E and to investigate the variation in $-\log I$ with the value of m.

RESULTS AND DISCUSSION

The results of the numerical integrations of

$$I = \int_0^T T^m \, e^{-E/RT} \, dT \qquad (5)$$

are shown in Tables 1—4 for $m = 1/2$, 1, 3/2, and 2, respectively. Most of the data are accurate to either four or five decimal places, about the the limit imposed by using $R = 1.9872$ cal mole^{-1} deg^{-1}, with the values being more accurate for lower values of E [16]. These data provide a basis for develop-

TABLE 1

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.	19.86134	27.26611	34.64479	42.00670	49.35691	56.69846	64.03334	71.36290
400.	14.09189	19.67393	25.23048	30.77058	32.29919	41.81929	47.33286	52.84122
500.	10.57779	15.06566	19.52857	23.97533	28.41077	32.83784	37.25845	41.67393
600.	8.20060	11.95859	15.69213	19.40980	23.11632	26.81457	30.50644	34.19325
700.	6.47827	9.71457	12.92691	16.12364	19.30938	22.48695	25.65823	28.82448
800.	5.16845	8.01319	10.83445	13.64034	16.43540	19.22239	22.00315	24.77893
900.	4.13578	6.67574	9.19265	11.69445	14.18555	16.66869	19.14566	21.61771
1000.	3.29859	5.59453	7.86783	10.12625	12.37412	14.61412	16.84801	19.07702

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.	18.62681	26.03062	33.40871	40.77022	48.12014	55.46147	62.79617	70.12559
400.	12.79611	18.37693	23.93271	29.47229	35.00052	40.52034	46.03368	51.54186
500.	9.23474	13.72113	18.18311	22.62923	27.06422	31.49093	35.91126	40.32652
600.	6.81909	10.57536	14.30782	18.02475	21.73072	25.42856	29.12011	32.80665
700.	5.06438	8.29874	11.50985	14.70573	17.89085	21.06795	24.23885	27.40480
800.	3.72662	6.56922	9.38910	12.19405	14.98841	17.77487	20.55520	23.33065
900.	2.66939	5.20701	7.72242	10.22318	12.71351	15.19606	17.67256	20.14423
1000.	1.81031	4.10372	6.37540	8.63268	10.87971	13.11907	15.35245	17.58105

TABLE 3

Values of $-\log \int_0^T T^m \, e^{-E/RT} \, dT$ 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.	17.39223	24.79511	32.17261	39.53373	46.88336	54.22447	61.55900	68.88828
400.	11.50027	17.07989	22.63492	28.17399	33.70184	39.22138	44.73449	50.24249
500.	7.89160	12.37654	16.83761	21.28311	25.71764	30.14401	34.56407	38.97911
600.	5.43746	9.19206	12.92346	16.63966	20.34510	24.04253	27.73376	31.42004
700.	3.65033	6.88281	10.09273	13.28778	16.47229	19.64893	22.81946	25.98511
800.	2.28459	5.12511	7.94367	10.74769	13.54137	16.32731	19.10723	21.88234
900.	1.20276	3.73813	6.25209	8.75183	11.24142	13.72339	16.19943	18.67073
1000.	0.32174	2.61273	4.88284	7.13902	9.38524	11.62396	13.85684	16.08504

TABLE 4

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

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.	16.15763	23.55957	30.93650	38.29723	45.64657	52.98747	60.32183	67.65097
400.	10.20437	15.78281	21.33710	26.87567	32.40315	37.92241	43.43530	48.94312
500.	6.54837	11.03190	15.49208	19.93697	24.37105	28.79707	33.21686	37.63168
600.	4.05571	7.80868	11.53905	15.25454	18.95945	22.65648	26.34739	30.03341
700.	2.23613	5.46679	8.67554	11.86978	15.05370	18.22987	21.40004	24.56539
800.	0.84237	3.68089	6.49816	9.30128	12.09430	14.87972	17.65923	20.43401
900.	−0.26410	2.26910	4.78166	7.28041	9.76926	12.25067	14.72626	17.19719
1000.	−1.16709	1.12157	3.39016	5.64528	7.89070	10.12881	12.36210	14.58899

ing numerical procedures that include non-isothermal methods which do not follow the Arrhenius behavior of the frequency factor. In that sense, they provide numerical approximations to the functions described by Segal [15].

Application of the Romberg algorithm to values of $-\log I$ obtained using 10, 20, 30, 40, and 50 subintervals resulted in values which were no more accurate than those obtained using 100 subintervals. This was true for each value of m. As was found previously, the Romberg acceleration of convergence does not seem practical as a substitute for using a large number of subintervals [16].

Functions of E and 1/T

It has previously been shown that for the temperature-independent frequency factor ($m = 0$), $-\log I$ can be related to the activation energy by

$$-\log I = ME + B \tag{6}$$

where M and B are constants and the temperature is constant. Further, for a given value of E, the relationship between $-\log I$ and temperature can be expressed as

$$-\log I = N(1/T) + D \tag{7}$$

where N and D are constants. The $-\log I$ values shown in Tables 1—4 fitted to these equations resulted in the regression parameters shown in Tables 5 and 6. It is readily apparent that these non-Arrhenius temperature integrals obey these relationships as well as do those where the frequency factor is independent of temperature [3,16].

Equations relating slopes and intercepts for a constant m

In the case of the tabulated values of the temperature integral for Arrhenius behavior, it was found that the slopes and intercepts of eqns. (6) and (7) varied in a systematic way. Thus, for $m = 0$, Gyulai and Greenhow used linear regression to establish relationships between the slopes or intercepts and E or T [3]. For example, in the equation

$$-\log I = ME + B \tag{6}$$

it was found that

$$M = K(1/T)^{L} \tag{8}$$

and

$$B = P\log(1/T) + Q \tag{9}$$

where K, L, P, and Q are constants. Thus, a numerical equation of the form

$$-\log I = K(1/T)^{L}E + \log(1/T)^{P} + Q \tag{10}$$

was obtained by making the equation for $-\log I$ as a function of E to reflect the variation of slope and intercept with temperature.

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	0.735546	2.15664	0.999999	0.735509	3.39061	0.999999
400	0.553375	2.46195	0.999998	0.553328	3.75699	0.999998
500	0.444048	2.69706	0.999997	0.443990	4.03921	0.999997
600	0.371148	2.88795	0.999995	0.371077	4.26839	0.999996
700	0.319148	3.04839	0.999994	0.318980	4.46104	0.999994
800	0.279979	3.18657	0.999992	0.279893	4.62770	0.999993
900	0.249574	3.30779	0.999991	0.249480	4.77263	0.999991
1000	0.225242	3.41566	9.999989	0.225139	4.90224	0.999990

	m = 3/2			m = 2		
	Slope (M)	—Intercept (B)	Corr. coeff.	Slope (M)	—Intercept (B)	Corr. coeff.
300	0.735473	4.62462	0.999999	0.735437	5.85867	0.999999
400	0.553281	5.05209	0.999998	0.553235	6.34726	0.999998
500	0.443933	5.38145	0.999997	0.443877	6.72379	0.999996
600	0.371011	5.64895	0.999996	0.370946	7.02965	0.999996
700	0.318905	5.87386	0.999994	0.318831	7.28686	0.999994
800	0.279809	6.06766	0.999993	0.279727	7.50852	0.999993
900	0.249388	6.23774	0.999992	0.249298	7.70310	0.999992
1000	0.225040	6.38914	0.999990	0.224943	7.87634	0.999991

Similarly, for

$$-\log I = N(1/T) + D \qquad (7)$$

it was found that

$$N = YE^{X} \qquad (11)$$

and

$$D = W \log E + U \qquad (12)$$

where X, Y, U, and W are constants. Equations (11) and (12) yield, by substitution into eqn. (7)

$$-\log I = YE^{X}(1/T) + \log E^{W} + U \qquad (13)$$

when the variation in slope and intercept with activation energy is included.

Using linear regression, similar numerical equations have been obtained in this work for each value of m used. Table 7 shows the values of the constants of eqns. (10) and (13) for the cases where $m = 0, 1/2, 1, 3/2,$ and 2. The values for $m = 0$ case are based on the previously published data for Arrhenius behavior [3,16]. The fit of all the data to equations (8)—(11) yielded correlation coefficients of 0.9999 or higher.

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	7095.95	3.69827	0.999916	7204.20	5.27479	0.999883
40	9285.36	3.59031	0.999950	9394.27	5.16980	0.999929
50	11473.31	3.50402	0.999967	11582.66	5.08542	0.999953
60	13660.47	3.43209	0.999976	13770.13	5.01483	0.999966
70	15847.15	3.37040	0.999982	15957.04	4.95412	0.999975
80	18033.51	3.31637	0.999986	18143.57	4.90083	0.999980
90	20219.63	3.26825	0.999989	20329.84	4.85332	0.999984
100	22405.57	3.22488	0.999991	22515.89	4.18044	0.999987
	m = 3/2			*m* = 2		
	Slope (*N*)	—Intercept (*D*)	Corr. coeff.	Slope (*N*)	—Intercept (*D*)	Corr. coeff.
30	7312.55	6.85163	0.999845	7420.99	8.42879	0.999803
40	9503.24	6.74950	0.999906	9612.28	8.32939	0.999880
50	11692.05	6.66696	0.999937	11801.48	8.24864	0.999919
60	13879.81	6.59766	0.999955	13989.53	8.18060	0.999942
70	16067.07	6.53825	0.999966	16176.88	8.12179	0.999956
80	18253.65	6.48537	0.999973	18363.75	8.06996	0.999966
90	20440.05	6.43845	0.999979	20550.28	8.02362	0.999972
100	22626.22	6.39604	0.999982	22736.56	7.98168	0.999977

The numerical equations of the form (10) or (13) permit interpolation of the data to give $-\log I$ values for any values of E and T. Therefore, using these equations, a table of $-\log I$ values at a large number of combinations of temperature and activation energy can be constructed without having to perform that number of integrations. It is also possible to quickly obtain a value of $-\log I$ at any desired conditions of T, E, and m.

TABLE 7

The constants of eqns. (10) and (13) obtained by linear regression

m	Eqn. (10)				Eqn. (13)			
	K	*L*	*P*	*Q*	*X*	*Y*	*W*	*U*
0	199.477	0.98258	1.92299	3.84257	0.96443	261.884	0.92462	—3.49132
1/2	199.832	0.98288	2.40749	3.80321	0.95595	273.489	0.90712	—5.04236
1	200.248	0.98325	2.89091	3.76614	0.94762	285.404	0.89004	—6.59430
3/2	200.615	0.98357	3.37412	3.72853	0.93943	297.632	0.87344	—8.14725
2	201.654	0.98444	3.85819	3.69304	0.93139	310.184	0.85754	—9.70148

Dependence of —log I on m

Since the $m = 0$ case was dealt with previously and this work covers the case where $m = 1/2$, 1, 3/2, and 2, it is now possible to examine in detail the dependence of $-\log I$ on m. Using the values of $-\log I$ at given values of E and T, linear regression was performed to relate $-\log I$ to m. The curve fit program tests several functions but the linear equation

$$-\log I = Am + C \tag{14}$$

where A and C are constants gave the best fit. In fact, for several of the series of data tested, the correlation coefficients were 1.00 ... and it was always above 0.99999. The value of the slope was almost equal to $\log T$ in each case. Furthermore, the values of the intercepts were simply the values of $-\log I$ at the same T and E that results when $m = 0$ [16]. The linear relationships of eqn. (14) also permit interpolation and extrapolation to include other values of m. For example, at $T = 300$ K and $E = 30$ kcal mole^{-1}, the relationship is

$$-\log I = -2.46908\, m + 21.09613 \tag{15}$$

with $r = 0.9999999$. Thus, if $m = -\frac{1}{2}$, the value predicted for $-\log I$ is 22.330684. The actual result of the numerical integration is 22.330314. Using the data shown in Tables 1—4 and those previously given [16], it is possible to obtain relationships to calculate $-\log I$ for any value of m. Then, using eqns. (10) and (13), one can obtain the values of $-\log I$ at other values of T and E. Therefore, the results presented here, taken in combination, permit evaluation of the temperature integral for all realistic values of E, T, and m.

CONCLUSION

The temperature integrals which have the frequency factor given by $A = A_m T^m$ have been evaluated. Relationships between $-\log I$ and E or $1/T$ have been established and their slopes and intercepts related to m, E, and T. The values of $-\log I$ are linear functions of m at given values of E and T. The necessary relationships are described to determine $-\log I$ for any values of E, T, and m.

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