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NUMERICAL INTEGRATION OF EULER'S INTEGRAL AND NUMERICAL RELATIONSHIPS INVOLVING *E* AND *T*

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ABSTRACT

Numerical integration has been carried out for

$$p(x)=\int_x^{\infty} x^{-2}\,e^{-x}\,dx$$

where $x = E/RT$ with $E = 20, 25, \ldots, 100$ kcal mole^{-1} and $T = 300, 350, \ldots, 1000$ K. Using the values of $-\log p(x)$, numerical equations have been obtained that enable calculations of $-\log p(x)$ at other values of E and T.

INTRODUCTION

The evaluation of kinetic parameters can be carried out for non-isothermal reactions that follow the rate law

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

where α is the fraction reacted, T is the temperature (K), β is the heating rate, A is the frequency factor, and n is the order. This evaluation hinges on obtaining values for the integral

$$I=\int_0^T e^{-E/RT}\,dT \tag{2}$$

by one of several means [1–10]. Tables of values of $-\log I$ are available [1,2] and several approximation techniques are widely used in thermoanalytical methods [1–10]. In an alternative treatment [11], the integrated function of

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α, $f(\alpha)$ is written as

$$f(\alpha)=\frac{AE}{\beta R}\,p(x) \tag{3}$$

where $x = E/RT$ and $p(x)$ represents the integral

$$p(x)=\int_{x}^{\infty} x^{-2}\,e^{-x}\,dx \tag{4}$$

The evaluation of this integral has recently been reviewed [12] and numerous approximation techniques by series have been proposed [12–14]. The standard table of values for $-\log p(x)$ is that of Doyle [13], although other tabulated values exist [14]. Doyle presents values of $-\log p(x)$ for $x = 10$–50 in integer units to three decimal places and gives differences for use in interpolation to other values of E and T. Zsako's table contains values for $-\log p(x)$ for t(C) = 100–430 and E = 10–66 kcal mole^{-1} (x ranging from 7.15 to 89.04). However, the $-\log p(x)$ values for $x < 50$ were obtained using the interpolation differences given by Doyle and they are not always accurate to even three decimal places. For example, with $t = 100$°C and $E = 50$ kcal mole^{-1}, $-\log p(x) = 32.95413$ by numerical integration compared with the reported value of 32.968 [14]. For $x > 50$, Zsako's values were obtained by means of the approximate formula

$$p(x)=e^{-x}\left(\frac{1}{x^{2}}-\frac{2}{x^{3}}\right) \tag{5}$$

Thus, there is no single table of highly accurate $-\log p(x)$ values covering the usually encountered ranges of E and T. In this work, we have carried out numerical integrations of eqn. (2) at regular intervals of E and T. These $-\log p(x)$ values are presented, as are numerical relationships to enable $-\log p(x)$ to be determined at any desired values of E and T.

METHODS

In order to provide a unified set of values for $-\log p(x)$ of higher accuracy than those available, numerical integration of

$$p(x)=\int_{x}^{\infty} x^{-2}\,e^{-x}\,dx \tag{4}$$

was carried out as previously described [15]. A Hewlett–Packard HP-34C programmable calculator was used employing the f SCI 3 accuracy level which results in values of $-\log p(x)$ that are accurate to five decimal places in most cases. It was determined [16] that the minimum upper limit of at least 218 was needed to produce full five-decimal accuracy with no change produced in the last digit by changing the upper limit. Therefore, the upper limit actually used was 250 as the approximation to infinity which would assure full accuracy. Numerical integrations were carried out for values of $E = 20, 25, \ldots, 100$ kcal mole^{-1} and $T = 300, 350, \ldots, 1000$ K. This range covers the values for E and T that are most useful in practical cases. Curve fitting was carried out by regression analysis as previously described [2].

RESULTS AND DISCUSSION

Numerical integration

As described earlier, the most widely cited tables of $-\log \mathrm{p}(x)$ are either based on approximation formulas [14] or do not include integral values of E and T [13]. The results of numerical integrations in this work provide values for $-\log \mathrm{p}(x)$ for an extended range of E and T values. The values shown in Table 1 are accurate to all five decimal places in most cases. The only exceptions are a few of the values for combinations of lower T and higher E. Where they are comparable, these values are in good agreement with those of Doyle [13] and appear more accurate than those based on approximate formulas [14].

Linear relationships

The relationship

$$-\log I = ME + B \qquad \text{(at constant } T\text{)} \tag{5}$$

has been shown to represent accurately the values of the temperature integral [eqn. (2)] at different values of E [2,10]. Similarly, the equation

$$-\log I = N(1/T) + D \qquad \text{(at constant } E\text{)} \tag{6}$$

has been shown to represent the relationship of the temperature integral as a function of T [2,10]. Therefore, an objective of this work was to determine equivalent expressions for $-\log \mathrm{p}(x)$ from the values obtained by numerical integration. Tables 2 and 3 present linear regression parameters for the equations

$$-\log \mathrm{p}(x) = ME + B \qquad \text{(at constant } T\text{)} \tag{7}$$

and

$$-\log \mathrm{p}(x) = N(1/T) + D \qquad \text{(at constant } E\text{)} \tag{8}$$

where M, B, N and D are constants obtained by performing linear regression on the values shown in Table 1. It is readily apparent that the values of $-\log \mathrm{p}(x)$ can be treated numerically in exactly the same way as $-\log I$ values can. In each case, the derived numerical equations are of equal accuracy to those for $-\log I$ [2] when the results of numerical integrations of equal accuracy are available.

TABLE 1

Values of $-\log \int_x^\infty x^{-2}\,\mathrm{e}^{-x}\,\mathrm{d}x$

T (K)	$E = 20$ kcal mole^{-1}	$E = 25$ kcal mole^{-1}	$E = 30$ kcal mole^{-1}	$E = 35$ kcal mole^{-1}	$E = 40$ kcal mole^{-1}	$E = 45$ kcal mole^{-1}	$E = 50$ kcal mole^{-1}	$E = 55$ kcal mole^{-1}
300	17.64559	21.47714	25.27475	29.04877	32.80544	36.54882	40.28160	44.00597
350	15.43411	18.74463	22.02141	25.27473	28.51084	31.73364	34.94597	38.14979
400	13.76087	16.68044	19.56648	22.42920	25.27475	28.10707	30.92897	33.74240
450	12.44011	15.06351	17.64556	20.20440	22.74613	25.27473	27.79293	30.30268
500	11.38897	13.76087	16.09964	18.41531	20.71396	22.99953	25.27475	27.54152
550	10.51508	12.68767	14.82732	16.94399	19.04371	21.13040	23.20676	25.27473
600	9.78080	11.78721	13.76087	15.71165	17.64556	19.56648	21.47712	23.37939
650	9.15440	11.02013	12.85327	14.66365	16.45721	18.23785	20.00823	21.77028
700	8.61317	10.35823	12.07088	13.76087	15.43411	17.09448	18.74463	20.38646
750	8.14037	9.78080	11.38897	12.97459	14.54353	16.09964	17.64556	19.18320
800	7.72345	9.27224	10.78896	12.28322	13.76087	15.22573	16.68044	18.12689
850	7.35272	8.82063	10.25661	11.67023	13.06729	14.45162	15.82584	17.19181
900	7.02068	8.41664	9.78081	11.12272	12.44815	13.76088	15.06351	16.35795
950	6.72135	8.05286	9.35279	10.63051	11.89181	13.14046	14.37905	15.60946
1000	6.44996	7.72347	8.96549	10.18539	11.38897	12.57995	13.76089	14.93366

T (K)	$E = 60$ kcal mole^{-1}	$E = 65$ kcal mole^{-1}	$E = 70$ kcal mole^{-1}	$E = 75$ kcal mole^{-1}	$E = 80$ kcal mole^{-1}	$E = 85$ kcal mole^{-1}	$E = 90$ kcal mole^{-1}	$E = 95$ kcal mole^{-1}	$E = 100$ kcal mole^{-1}
300	47.72323	51.43455	55.14080	58.84268	62.54075	66.23547	69.92722	73.71632	77.30304
350	41.34655	44.53744	47.72325	50.90470	54.08235	57.25666	60.42801	63.59671	66.76304
400	36.54881	39.34931	42.14478	44.93590	47.72323	50.50727	53.28830	56.06669	58.84271
450	32.80543	35.30230	37.79415	40.28166	42.76538	45.24578	47.72323	50.19804	52.67049
500	29.80133	32.05527	34.30420	36.54881	38.78964	41.02715	43.26172	45.49365	47.72323
550	27.33575	29.39091	31.44109	33.48694	35.52903	37.56781	39.60364	41.63686	43.66771
600	25.27475	27.16424	29.04876	30.92897	32.80543	34.67858	36.54880	38.41641	40.28165
650	23.52541	25.27473	27.01908	28.75913	30.49543	32.22843	33.95851	35.68597	37.41108
700	22.02141	23.65055	25.27475	26.89463	28.51079	30.12365	31.73360	33.34094	34.94593
750	20.71396	22.23894	23.75897	25.27473	26.78676	28.29550	29.80133	31.30455	32.80543
800	19.56648	21.00031	22.42920	23.85383	25.27475	26.69236	28.10707	29.51919	30.92897
850	18.55095	19.90434	21.25280	22.59702	23.93751	25.27473	26.60905	27.94078	29.27017
900	17.64557	18.92744	20.20440	21.47712	22.74613	24.01188	25.27475	26.53500	27.79293
950	16.83307	18.05095	19.26393	20.47268	21.67773	22.87953	24.07843	25.27474	26.46873
1000	16.09966	17.25994	18.41290	19.56650	20.71398	21.85821	22.99955	24.13830	25.27475

TABLE 2

Regression parameters for $-\log \int_x^\infty x^{-2}\, \mathrm{e}^{-x}\, \mathrm{d}x = ME + B$

T (K)	Slope (M)	Intercept (B)	Corr. Coeff.
300	0.744976	2.945656	0.999990
350	0.640533	2.830029	0.999986
400	0.562450	2.717520	0.999981
450	0.501744	2.616388	0.999976
500	0.453117	2.530608	0.999972
550	0.413352	2.451196	0.999966
600	0.380210	2.378966	0.999960
650	0.352163	2.312737	0.999954
700	0.328119	2.251629	0.999948
750	0.307278	2.194926	0.999941
800	0.289038	2.142059	0.999933
850	0.272942	2.092555	0.999926
900	0.258631	2.046037	0.999918
950	0.245825	2.002160	0.999910
1000	0.234294	1.960664	0.999901

TABLE 3

Regression parameters for $-\log \int_x^\infty x^{-2}\, \mathrm{e}^{-x}\, \mathrm{d}x = N(1/T) + D$

E (kcal mole^{-1})	Slope (N)	Intercept (D)	Corr. Coeff.
20	4805.66	1.720657	0.999893
25	5902.56	1.898619	0.999926
30	6997.84	2.046252	0.999946
35	8092.47	2.172223	0.999959
40	9186.68	2.282111	0.999968
45	10280.58	2.379608	0.999974
50	11374.25	2.467235	0.999979
55	12467.79	2.546764	0.999982
60	13561.18	2.619615	0.999985
65	14654.49	2.686803	0.999987
70	15747.98	2.748537	0.999988
75	16840.88	2.807333	0.999990
80	17934.00	2.861850	0.999991
85	19027.07	2.913130	0.999992
90	20120.10	2.961558	0.999993
95	21235.85	2.974221	0.999996
100	22306.09	3.050974	0.999994

General equations

The data shown in Table 2 have been used to evaluate K and L in the equation

$$M = K(1/T)^L \tag{9}$$

and to evaluate P and Q in the equation

$$B = P\log(1/T) + Q \tag{10}$$

where M and B are the slope and intercept of eqn. (7) and K, L, P and Q are constants. The values obtained by linear regression are $K = 176.896$, $L = 9.117449$, $P = 1.897710$, and $Q = 7.652085$. Thus, the equation

$$-\log p(x) = K(1/T)^L E + \log(1/T)^P + Q \tag{11}$$

can be used to evaluate $-\log p(x)$ at any values of E and T. Similarly, the data shown in Table 3 are used to evaluate X and Y in the equation

$$N = YE^X \tag{12}$$

and W and U in the equation

$$D = W\log E + U \tag{13}$$

where N and D are the slope and intercept of eqn. (8) and X, Y, W and U are constants. Using linear regression, the values $Y = 270.237$, $X = 0.957160$, $W = 1.898343$, and $U = -0.755620$ are obtained. These parameters are used to establish the equation

$$-\log p(x) = YE^X(1/T) + \log E^W + U \tag{14}$$

Equations (11) and (14) provide rapid evaluation of $-\log p(x)$ at any desired values of E and T without the necessity for performing numerical integrations or approximations by series. Consequently, these equations may provide functional bases for non-isothermal kinetic methods [17]. It should be pointed out, however, that eqns. (11) and (14) do not appear to yield values of $-\log p(x)$ which are as accurate as the $-\log I$ values obtained using equations of the same form [15]. We have not explored the reason for this difference.

CONCLUSION

This work has provided a more accurate table of values of $-\log p(x)$ than was previously available. We have used linear regression to establish the constants M, B, N and D for using

$$-\log p(x) = ME + B \tag{7}$$

and

$$-\log p(x) = N(1/T) + D \tag{8}$$

to calculate $-\log p(x)$ for any desired E and T. Also, the slopes and intercepts of eqns. (7) and (8) have been determined as functions of $1/T$ and E so that two general numerical equations that permit $-\log p(x)$ to be evaluated at any desired E and T values have been obtained.

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