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EQUATIONS FOR THE RAPID EVALUATION OF GENERAL TEMPERATURE INTEGRALS IN NON-ISOTHERMAL KINETIC ANALYSIS

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ABSTRACT

Integrals of the form $\int_0^T A_m T^m e^{-E/RT} dT$ have been evaluated for integer and fractional values of $m = b - 2$. The results of the numerical integration are presented for Arrhenius integrals having negative as well as positive exponents. Equations have been derived which relate m to the natural logarithm of the p(x) function. Methods for the rapid evaluation of general temperature integrals for any combination of m and x, from four different approximations, are also presented.

INTRODUCTION

Non-isothermal methods have been widely used for the evaluation of kinetic parameters of decomposition reactions [1–7]. The rate of a decomposition process can be described [5] as the product of two separate functions of temperature and conversion as

$$\frac{d\alpha}{dt} = k_{(T)} f(\alpha) \tag{1}$$

where the function $k_{(T)}$ is temperature dependent and f(α) is the conversion function which depends on the reaction mechanism. Earlier workers [8] have shown that for a series of isothermal mass-loss measurements, plots of log t, the time taken to reach a percentage mass loss, vs. $1/T$, the reciprocal absolute temperature, are linear. This shows that the temperature dependence is of the Arrhenius type, and therefore $k_{(T)}$ can be considered as the rate constant, k

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

where A and E are the Arrhenius pre-exponential factor and activation energy respectively, and R is the gas constant.

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Substituting in eqn. (1), we get

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\ \mathrm{e}^{-E/RT}\mathrm{f}(\alpha) \tag{3}$$

For a linear heating rate ϕ, eqn. (3) becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\phi}\mathrm{e}^{-E/RT}\mathrm{f}(\alpha) \tag{4}$$

Equation (4) may be considered as the general equation connecting E, A and n [when $\mathrm{f}(\alpha)$ is assumed as $(1-\alpha)^n$].

Most of the existing methods to evaluate the kinetic parameters utilize eqn. (4) in three different approaches [9], viz. integral, differential and approximation. The most accurate among them are the integral methods [5,10].

On rearranging and integrating eqn. (4) between the limits of $\alpha = 0$ at T_i and α at T, we get

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A}{\phi}\int_{T_i}^T \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{5}$$

where $\int_0^\alpha[\mathrm{d}\alpha/\mathrm{f}(\alpha)]$ is the conversion integral. The lower limit T_i is generally taken as zero for the ease of integration [11]. The integral form of the LHS is $\mathrm{g}(\alpha)$ and thus, eqn. (5) can be written as

$$\mathrm{g}(\alpha) = \frac{A}{\phi}\int_0^T \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{6}$$

In the integral methods, it is usually assumed that the pre-exponential factor, A is temperature independent [3,4]. However, the transition state theory predicts that A is temperature dependent [12,13]. Therefore, eqn. (6) becomes

$$\mathrm{g}(\alpha) = \frac{A_{(T)}}{\phi}\int_0^T \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{7}$$

The temperature dependence of A can be represented as

$$A_{(T)} = A_m T^m \tag{8}$$

Substituting eqn. (8) in eqn. (7), we get

$$\mathrm{g}(\alpha) = \frac{A_m T^m}{\phi}\int_0^T \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{9}$$

A_m is now temperature independent.

There are two general cases where $m = 0.5$ and 1.0 for solid state reactions. However, other possibilities have also been found where m varies from -4 to $+2$ [14]. When $x = E/RT$ is substituted, eqn. (9) becomes

$$\mathrm{g}(\alpha) = \frac{A_m}{\phi}\left(\frac{E}{R}\right)^{m+1}\int_x^\infty \left(\frac{\mathrm{e}^{-x}}{x^{m+2}}\right)\mathrm{d}x \tag{10}$$

when $b=(m+2)$ is substituted, eqn. (10) reverts to the standard form of the incomplete gamma function, $\int_x^\infty \frac{e^{-u}}{u^b} du$, viz.

$$g(\alpha) = \frac{A_b}{\phi}\left(\frac{E}{R}\right)^{b-1} p(x) \tag{11}$$

On rearranging and taking logarithms, eqn. (11) becomes

$$\ln g(\alpha) - \ln p(x) = \ln \frac{A_b}{\phi}\left(\frac{E}{R}\right)^{b-1} \tag{12}$$

Thus E and A can be calculated, if the values of $g(\alpha)$ and $p(x)$ are known.

The values of the temperature integral, $p(x)$ can be evaluated from simple approximation [15–17], numerical integration [18–20] and series solutions [21–25]. The most important among the series solutions are Scholmilch, semiconvergent, etc. The series solutions for $p(x)$ with $b=2$ have been reviewed by Wendlandt and co-workers [26]. Segal [27] has derived approximations of the temperature integrals by assuming different positive values of b. Several other studies were also reported for evaluating temperature integral values with $b = 0$, $\pm 1/2$, ± 1, $\pm 3/2$ and ± 2 using different approaches [28–31].

Recent papers [32–34] have compared different approximations and shown that a Scholmilch series is the most accurate for $x > 15$. We have also [35] proposed a new series approximation for the $p(x)$ function which gave very close values to those of the Scholmilch approximation. In the present study, we have attempted to evaluate the $p(x)$ values from four different approximations for the range of values of $b = -2$ (0.5) $+4$ [or $m = -4$ (0.5) $+2$] and $x = 15$ (5) 60. The computation and curve fits were done by a CDC computer using a FORTRAN IV program.

RESULTS AND DISCUSSION

It has been found that the values of $p(x)$ evaluated from Scholmilch or similar type of series are more accurate than those from asymptotic expansions, and therefore the following equations are employed in this work

1. Scholmilch approximation [23]

$$p(x) = \frac{e^{-x}}{x^b}\left[1 - \frac{a_1}{(x+1)} + \frac{a_2}{(x+1)(x+2)} - \frac{a_3}{(x+1)\dots(x+3)} + \frac{a_4}{(x+1)\dots(x+4)} - \frac{a_5}{(x+1)\dots(x+5)} + \dots\right] \tag{13}$$

Where $a_1 = b$, $a_2 = b^2$, $a_3 = b^3 + b$, $a_4 = b^4 + 4b^2 - b$ and $a_5 = b^5 + 10b^3 + 5b^2 + 8b$.

2. Semiconvergent series

$$p(x)=\frac{e^{-x}}{x^{b}}\left[1-\frac{b}{x}+\frac{b(b+1)}{x^{2}}-\frac{b(b+1)(b+2)}{x^{3}}\right.$$
$$\left.+\frac{b(b+1)\ldots(b+3)}{x^{4}}-\frac{b(b+1)\ldots(b+4)}{x^{5}}+\ldots\right] \quad (14)$$

3. New series approximation [35]

$$p(x)=\frac{e^{-x}}{x^{b}}\left[1-\frac{b}{(x+b+1)}-\frac{b(b^{2}-1)}{(b-1)(x+1)(x+2)(x+b+1)}\right.$$
$$+\frac{b^{2}(b^{3}-1)}{(b-1)(x+1)\ldots(x+3)(x+b+2)}$$
$$-\frac{b^{3}(b^{4}-1)}{(b-1)(x+1)\ldots(x+4)(x+b+3)}$$
$$\left.+\frac{b^{4}(b^{5}-1)}{(b-1)(x+1)\ldots(x+5)(x+b+4)}-\ldots\right] \quad (15)$$

4. Three term approximation [35]

$$p(x)=\frac{e^{-x}}{x^{b}}\left[1-\frac{b}{(x+b+1)}-\frac{(b^{2}+1)}{(x+1)(x+2)(x+b+1)}\right] \quad (16)$$

For the computation of $p(x)$, expansions up to six terms were used in eqns. (13), (14) and (15). However, in eqn. (16) only three terms are taken because the third term represents the approximate sum of all the terms beyond the second in eqn. (15).

In order to prepare the complete set of numerical tables for $p(x)$, $x = 15$ (5) 60 and $b = -2$ (0.5) $+4$ were chosen. By introducing the numerical values of x and b in eqns. (13), (14), (15) and (16), values of $-\ln p(x)$ were computed. A total of 120 sets of values thus obtained from the four equations are given in Tables 1, 2, 3 and 4 respectively. From these tables, it can be seen that the $-\ln p(x)$ values for all the four approximations are very close.

Dependence of $-\ln p(x)$ on b

Using the above tabulated values of $-\ln p(x)$, linear plots were drawn for $-\ln p(x)$ vs. b for different values of x. This linear relation can be represented as

$$-\ln p(x)=M+Nb \quad (17)$$

TABLE 1

Values of $-\ln p(x)$ from the Scholmilch approximation

b	$x=15$	$x=20$	$x=25$	$x=30$	$x=35$	$x=40$	$x=45$	$x=50$	$x=55$	$x=60$
−2.0	9.450968	13.908701	18.482333	23.130987	27.832192	32.572262	37.342245	42.135965	46.948978	51.777984
−1.5	10.839703	15.432385	20.112309	24.848634	29.624435	34.429421	39.256862	44.102118	48.961854	53.833589
−1.0	12.227420	16.955480	21.741904	26.566013	31.416481	36.286428	41.171359	46.068174	50.974648	55.889126
−0.5	13.614170	18.478011	23.371130	28.283133	33.208334	38.143287	43.085737	48.034134	52.987363	57.944596
+0.5	16.384955	21.521468	26.371130	31.716622	36.791482	41.856571	46.914149	51.965773	57.012560	62.055339
1.0	17.769077	23.042433	28.256716	33.433006	38.582786	43.713004	48.828188	53.931455	59.025043	64.110613
1.5	19.152409	24.562925	29.884585	35.149158	40.373915	45.569300	50.742117	55.897048	61.037453	66.165825
2.0	20.534989	26.682952	31.512141	36.865086	42.164874	47.425463	52.655939	57.862553	63.049789	68.220974
2.5	21.916859	27.602535	33.139395	38.580794	43.955668	49.281500	54.569657	59.827972	65.062052	70.276062
3.0	23.298059	29.121693	34.766358	40.296289	45.746299	51.137402	56.483272	61.793306	67.074245	72.331090
3.5	24.678633	30.640445	36.393038	42.011578	47.536772	52.993184	58.396786	63.758557	69.086368	74.386058
4.0	26.058628	32.158811	38.019447	43.726660	49.327092	54.848843	60.310201	65.723726	71.098422	76.440967

TABLE 2

Values of $-\ln p(x)$ from the semiconvergent series

b	$x=15$	$x=20$	$x=25$	$x=30$	$x=35$	$x=40$	$x=45$	$x=50$	$x=55$	$x=60$
−2.0	9.450924	13.908690	18.482329	23.130986	27.832191	32.572261	37.342245	42.135964	46.948978	51.777984
−1.5	10.839681	15.432379	20.112307	24.848633	29.624435	34.429421	39.256862	44.102118	48.961854	53.833589
−1.0	12.227411	16.955478	21.741903	26.566013	31.416481	36.286428	41.171359	46.068174	50.974648	55.889126
−0.5	13.614167	18.478010	23.371130	28.283133	33.208334	38.14286	43.085737	48.034143	52.987363	57.944596
+0.5	16.384964	21.521470	26.628525	31.716622	36.791482	41.856571	46.914149	51.965773	57.012560	62.055339
1.0	17.769117	23.042444	28.256718	33.433007	38.582786	43.713004	48.828183	53.931455	59.025043	64.110613
1.5	19.152528	24.562946	29.884590	35.149160	40.373916	45.569300	50.742117	55.897048	61.037453	66.165825
2.0	20.535284	26.083004	31.512155	36.865090	42.164876	47.425464	52.655940	57.862553	63.049789	68.220974
2.5	21.917490	27.602649	33.139425	38.580804	43.955671	49.281498	54.569658	59.827972	65.062053	70.276062
3.0	23.299280	29.121915	34.766416	40.296309	45.746307	51.137406	56.483274	61.793306	67.074246	72.331090
3.5	24.680829	30.640844	36.393143	42.011613	47.536786	52.993190	58.396789	63.758558	69.086369	74.386058
4.0	26.062356	32.159487	38.019625	43.726725	49.327115	54.848854	60.310206	65.723729	71.098424	76.440968

TABLE 3

Values of $-\ln p(x)$ from the new series approximation

b	$x=15$	$x=20$	$x=25$	$x=30$	$x=35$	$x=40$	$x=45$	$x=50$	$x=55$	$x=60$
−2.0	9.450703	13.908613	18.482295	23.130968	27.832181	32.572255	37.342241	42.135962	46.948976	51.77798
−1.5	10.839613	15.432355	20.112297	24.848628	29.624432	34.429415	39.256861	44.102117	48.961853	53.833589
−1.0	12.227399	16.955473	21.741902	26.566012	31.416481	36.286428	41.171358	46.068174	50.964648	55.889126
−0.5	13.614166	18.478010	23.371130	28.283132	33.208334	38.143287	43.085737	48.034134	52.987363	57.944596
+0.5	16.384964	21.521472	26.628526	31.716623	36.791483	41.856572	46.914150	51.965773	57.012560	62.055339
1.0	17.769100	23.042446	28.256720	33.433008	38.582786	43.713004	48.828188	53.931453	59.025044	64.110613
1.5	19.152435	24.562936	29.884590	35.159161	40.373917	45.569301	50.742118	55.897048	61.037453	66.165825
2.0	20.534982	26.082952	31.512142	36.865086	42.164875	47.425464	52.655940	57.862553	63.049789	68.220974
2.5	21.916749	27.602500	33.139381	38.580787	43.955664	49.281494	54.569655	59.827971	65.062057	70.276062
3.0	23.297713	29.121583	34.766311	40.296266	45.746286	51.137394	56.483267	61.793302	67.074243	72.331088
3.5	24.677772	30.640186	36.392931	42.011525	47.536743	52.993166	58.396774	63.758549	69.086363	74.386054
4.0	26.056628	32.158255	38.019229	43.726561	49.327034	54.848809	60.310179	65.723711	71.098412	76.440960

TABLE 4

Values of $-\ln p(x)$ from the three term approximation

b	$x=15$	$x=20$	$x=25$	$x=30$	$x=35$	$x=40$	$x=45$	$x=50$	$x=55$	$x=60$
−2.0	9.451262	13.908878	18.482440	23.131057	27.832239	32.572295	37.342269	42.135983	46.948992	51.777995
−1.5	10.840086	15.432578	20.112419	24.848701	29.624480	34.429450	39.256884	44.102135	48.961866	53.833599
−1.0	12.227794	16.74200	21.742002	26.566072	31.416519	36.286454	41.171377	46.068188	50.974659	55.889134
−0.5	13.614474	18.478152	23.371206	28.283178	33.208364	38.143307	43.085752	48.034145	52.987371	57.944602
+0.5	16.385084	21.521525	26.628555	31.716640	36.791493	41.856579	46.914155	51.965777	57.012562	62.055341
1.0	17.769135	23.042458	28.256726	33.433011	38.582789	43.713005	48.823189	53.931456	59.025044	64.110614
1.5	19.152435	24.562926	29.884581	35.149156	40.373912	45.569297	50.742115	55.897046	61.037451	66.165824
2.0	20.535033	26.082925	31.512134	36.865078	42.164865	47.425458	52.655935	57.862549	63.049786	68.220972
2.5	21.916975	27.602556	33.139394	38.580787	43.955661	49.281490	54.569651	59.827967	65.062049	70.276059
3.0	23.298301	29.121757	34.766375	40.296291	45.746295	51.137398	56.483267	61.793301	67.074241	72.331086
3.5	24.679051	30.640580	36.393085	42.011594	47.536776	53.993183	58.396783	63.758554	69.086365	74.386055
4.0	26.059258	32.159036	38.019536	43.726703	49.327107	54.848849	60.310202	65.723725	71.098421	76.440965

TABLE 5

Curve fit constants for $-\ln p(x)$ vs. b plots for eqn. (13)

x	Slope (N)	Intercept (M)	r
15	2.767891	14.995273	0.99999956
20	3.041675	19.997173	0.99999987
25	3.256187	24.998121	0.99999994
30	3.432618	29.998661	0.99999997
35	3.582490	34.998997	0.99999998
40	3.712770	39.999222	0.99999999
45	3.827998	44.999938	0.99999999
50	3.931299	49.999465	0.99999999
55	4.024912	54.999576	1.00000000
60	4.110502	59.999641	1.00000000

A total of 40 sets of values of slope, intercept and correlation coefficients were calculated and these values are given in Tables 5–8. From these tables it can be seen that the value of the slope increases with increase in x. Similarly, intercepts also show the same increasing trend with increasing x. Another interesting observation is that the intercepts obtained from the curve fits tend to the theoretical values of x as the value of x increases. The correlation coefficients also show the same trend. In all the cases studied the correlation coefficients are almost unity, and therefore the four approximations are equally applicable for the computation of $p(x)$ when $x > 15$.

Relation between slopes and x

Using the computed values of slope, several curve fits were tried with x. It was found that the slope vs. ln x plot is linear. The relation can be

TABLE 6

Curve fit constants for $-\ln p(x)$ vs. b plots for eqn. (14)

x	Slope (N)	Intercept (M)	r
15	2.768340	14.995461	0.99999966
20	3.041750	19.997257	0.99999988
25	3.256209	24.998129	0.99999995
30	3.432626	29.998663	0.99999997
35	3.582492	34.998998	0.99999998
40	3.712777	39.999222	0.99999999
45	3.828000	44.999379	0.99999999
50	3.931299	49.999492	0.99999999
55	4.024912	54.999576	1.00000000
60	4.110502	59.999642	1.00000000

TABLE 7

Curve fit constants for $-\ln p(x)$ vs. b plots for eqn. (15)

x	Slope (N)	Intercept (M)	r
15	2.767717	14.995155	0.99999960
20	3.041627	19.997136	0.99999987
25	3.256168	24.998106	0.99999994
30	3.432609	29.998653	0.99999997
35	3.582484	34.998993	0.99999999
40	3.712767	39.999219	0.99999999
45	3.827996	44.999376	0.99999999
50	3.931298	49.999490	0.99999999
55	4.024911	54.999576	0.99999999
60	4.110501	59.999641	0.99999999

TABLE 8

Curve fit constants for $-\ln p(x)$ vs. b plots for eqn. (16)

x	Slope (N)	Intercept (M)	r
15	2.767898	14.995518	0.99999959
20	3.041663	19.997287	0.99999987
25	3.256175	24.998182	0.99999994
30	3.432608	29.998697	0.99999997
35	3.582481	34.999021	0.99999998
40	3.712763	39.999237	0.99999999
45	3.827993	44.999389	0.99999999
50	3.931295	49.999500	0.99999999
55	4.024909	54.999582	0.99999999
60	4.110499	59.999647	0.99999999

represented as

$$\text{slope } (N) = N_1 + N_2 \ln x \tag{18}$$

The values of N_1, N_2 and the correlation coefficients for the four approximations are given in Table 9. On substituting the numerical values in eqn.

TABLE 9

Results of slope vs. $\ln x$ plots

	Scholmilch	Semiconvergent	New series	Three term
Slope N_2	0.969609	0.969383	0.969703	0.969609
Intercept N_1	0.137537	0.138402	0.137178	0.137533
r	0.9999840	0.9999829	0.9999844	0.9999840

TABLE 10

Results of intercept vs. x plots

	Scholmilch	Semiconvergent	New series	Three term
Slope M_2	1.000079	1.000077	1.000081	1.000075
Intercept M_1	−0.004414	−0.004303	−0.004501	−0.004217
r	1.00000000	1.0000000	0.999999998	0.999999997

(18), the following equations were obtained for the data from the four approximations

Scholmilch $\quad (N) = 0.137537 + 0.969609 \ln x \quad (19)$

Semiconvergent $\quad (N) = 0.138402 + 0.969383 \ln x \quad (20)$

New series $\quad (N) = 0.137178 + 0.969703 \ln x \quad (21)$

Three term $\quad (N) = 0.137533 + 0.969609 \ln x \quad (22)$

Relation between intercepts and x

A similar examination of the data showed that the intercept, M varies linearly with x. The relation can be represented as

$$\text{Intercept } (M) = M_1 + M_2 x \tag{23}$$

The numerical values of slope M_2 and intercept M_1 along with the correlation coefficients are given in Table 10. Substituting the numerical values of M_1 and M_2, we get the following equations for the four approximations

Scholmilch $\quad (M) = -0.004414 + 1.000079x \quad (24)$

Semiconvergent $\quad (M) = -0.004303 + 1.000077x \quad (25)$

New series $\quad (M) = -0.004501 + 1.000081x \quad (26)$

Three term $\quad (M) = -0.004217 + 1.000075x \quad (27)$

For all the plots, the correlation coefficients are very high, indicating the goodness of the fits.

Equations relating slopes and intercepts

Substituting eqns. (18) and (23) in eqn. (17), we get the relation showing the total dependence of $-\ln p(x)$ and x. The final form of the equation can be represented as

$$-\ln p(x) = M_1 + M_2 x + (N_1 + N_2 \ln x)b \tag{28}$$

Substituting the numerical values of slopes M_2 and N_2 and intercepts M_1 and N_1 in eqn. (28) we get the following equations for $-\ln p(x)$

Scholmilch

$$-\ln p(x) = -0.004414 + 1.000079x + (0.137537 + 0.969609\ln x)b \ldots \quad (29)$$

Semiconvergent

$$-\ln p(x) = -0.004303 + 1.000077x + (0.138402 + 0.969383\ln x)b \ldots \quad (30)$$

New series

$$-\ln p(x) = -0.004501 + 1.000081x + (0.137178 + 0.969703\ln x)b \ldots \quad (31)$$

Three term

$$-\ln p(x) = -0.004217 + 1.000075x + (0.137533 + 0.968709\ln x)b \ldots \quad (32)$$

When $b = 2$, eqns. (29)–(32) become the Arrhenius temperature integral.

The validity of these equations was tested by comparing the $-\ln p(x)$ values calculated using eqns. (29)–(32) with the theoretical values of $-\ln p(x)$. The percentage deviations from the theoretical values (for $b = 2$) are 5.670×10^{-2}, 5.528×10^{-2}, 5.796×10^{-2} and 5.629×10^{-2}, respectively, for eqns. (29), (30), (31) and (32), when $x = 15$. Similarly, the percentage deviation from the theoretical values are 8.424×10^{-3}, 5.013×10^{-3}, 8.301×10^{-3} and 8.496×10^{-3}, respectively, for eqns. (29), (30), (31) and (32), when $x = 60$. Thus, the theoretical as well as the computed values of the temperature integrals are very close for the four approximations employed in this study.

CONCLUSIONS

In the present study, the temperature integrals evaluated with non-integer values of b have been compared for different series approximations. Since E and $1/T$ are separate linear functions of $\ln p(x)$, the combined dependence of $\ln p(x)$ on x ($x = E/RT$) for different values of b has been established and equations are presented to relate $-\ln p(x)$ accurately to the value of b, using four series approximations.

Most of the equations derived are only for the temperature integral, where $b = 2$. In this study it is observed that the general series solutions and the Scholmilch series are equally applicable in the evaluation of $p(x)$ functions for values of b ranging from -2 to $+4$. The values of $p(x)$ computed from the closed form three term approximation, derived from the general series solution, also show good agreement with those from the Scholmilch or series approximations.

An important aspect of this study is that $-\ln p(x)$ can be rapidly determined for any value of x and b by simple substitution in any of the eqns. (29)–(32) or from the tables. Thus, it is possible to obtain the values of the general temperature integrals at any set of conditions for the analysis of non-isothermal kinetic data.

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